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THE M.W. KELLOGG COMPANY

Petroleum and Chemical Research Department

PROGRESS REPORT

ARCTIC RUBBER

U.S. Army Contract DA-44-109-qm-222
Project No. 7-93-15-604
For the Period April-July, 1953

August 1, 1953

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Petroleum and Chemical Research Department
Laboratory Division, Jersey City, New Jersey

PROGRESS REPORT

Subject: Arctic Rubber - U.S. Army Contract DA-44-109-qm-222
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Period Covered: April 1, 1953 to July 31, 1953

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Previous Reports on this Subject:

RL-50-139	dated	November 1, 1950
RL-51-146	"	February 1, 1951
RL-51-156	"	April 1, 1951
RL-51-163	"	July 1, 1951
RL-51-174	"	October 1, 1951
RL-52-183	"	February 1, 1952
RL-52-195	"	May 1, 1952
RL-52-209	"	August 1, 1952
RL-52-248	"	October 1, 1952
RL-53-259	"	January 1, 1953
RL-53-274	"	April 1, 1953

Approved:

E F Schwarzenbek

E.F. SCHWARZENBEK

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I. Introduction

A. Purpose of the Project

The primary purpose of this project is the development of a fluorine containing oil- and fuel-resistant elastomer which will retain its rubbery properties between -70°F. and +160°F. A more recent objective is the pilot plant production and large scale evaluation of the more promising elastomers, with special emphasis on the polymer currently designated by M.W. Kellogg as "X-300 Rubber."

B. Research Program

To achieve this goal, the M.W. Kellogg Company has been authorized by the Quartermaster Corps to conduct a broad investigation of fluorocarbon polymers involving (1) monomer synthesis; (2) polymer preparation; and (3) polymer evaluation. Emphasis has been placed upon polymer preparation and especially upon the copolymerization of fluoroolefins and fluoro-chloro-olefins among themselves and with olefinic and diolefinic hydrocarbons.

Monomer synthesis at Kellogg has been restricted to products arising from the thermal dimerization of $CF_2=CFCl$, namely, $CF_2=CF-CF=CF_2$, $CF_2-CF=CF-CF_2$, and $CF_3-CF=CF_2$. Where feasible, the preparation of other monomers, e.g., $CF_2=CF_2$ and $CF_2=CHF$, has also been undertaken in these laboratories. For the most part, however, monomers not available commercially have been requested from Dr. Paul Tarrant of the University of Florida, Dr. Aldrich Syverson of the Ohio State University, and Dr. W.T. Miller of Cornell University, or obtained on an exchange basis from Minnesota Mining and Manufacturing Company.

Polymer preparation has proceeded through four phases: (a) exploratory copolymerization of new monomer pairs; (b) determination of the relative reactivities of monomers successfully copolymerized into elastomers; (c) synthesis of pound batches of these elastomers in several comonomer ratios for evaluation; and (d) pilot plant production of one elastomer (Kellogg "X-300 Rubber") which is of interest to the Quartermaster not so much as an Arctic Rubber but more precisely as an acid- and oxidant-resistant elastomer for protective suits, gloves, and boots. A new phase, initiated during the present quarter, will involve the testing of small samples of unvulcanized, rubbery polymers, obtained from exploratory work, for oil-resistance and low temperature flexibility. This testing program will be carried on at the Quartermaster Depot in Philadelphia.

Recently, a program has been initiated for comparing all rubbery products obtained in exploratory work as to oil- and fuel-resistance and low temperature flexibility. Small samples (1-2 g.) of the raw polymer will be subjected to the Gehman torsional stiffness test and the solvent swell test in ASTM Reference Fuel No. 2.

Polymer compounding, testing, and evaluation has been carried forward most capably by Mr. C.B. Griffis and his staff at the Philadelphia Quartermaster Depot. The development of uses for X-300 has been the joint responsibility of Mr. Griffis and the Kellogg Applications Laboratory.

C. Past Progress

1. Quarters completed as of April 1, 1953: 11
2. Monomers available for copolymerization: 44

   a. Purchased: 18
   b. Minnesota Mining & Mfg. Co: 3
   c. Dr. Tarrant: 10
   d. Dr. Syverson: 7
   e. M.W. Kellogg Co: 6

3. Copolymer systems investigated: 236
   (where the numbers refer to the monomers listed in section III-A, below):

   1-2, 1-2-4, 1-2-9, 1-2-11, 1-2-14, 1-2-21, 1-2-22, 1-2-23, 1-2-24, 1-2-29, 1-2-30, 1-2-31, 1-2-35, 1-2-40, 1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 1-9, 1-12, 1-13, 1-14, 1-16, 1-17, 1-18, 1-19, 1-20, 1-21, 1-22, 1-23, 1-25, 1-27, 1-28, 1-30, 1-35, 1-36, 1-37, 1-39, 1-41, 2-3, 2-4, 2-6, 2-8, 2-9, 2-12, 2-13, 2-15, 2-16, 2-17, 2-18, 2-19, 2-21, 2-22, 2-23, 2-24, 2-28, 2-29, 2-30, 2-32, 2-34, 2-35, 2-37, 2-38, 2-39, 3-4, 3-7, 3-9, 3-14, 3-18, 3-19, 3-20, 3-21, 3-22, 3-23, 3-24, 3-25, 3-30, 3-32, 4, 4-5, 4-6, 4-8, 4-9, 4-10, 4-11, 4-12, 4-14, 4-15, 4-17, 4-19, 4-20, 4-21, 4-22, 4-24, 4-25, 4-28, 4-29, 4-32, 4-35, 4-37, 4-39, 4-41, 5-9, 6-8, 6-9, 6-30, 6-37, 6-41, 7-35, 7-37, 7-41, 8-13, 8-24, 8-35, 8-37, 8-41, 9, 9-12, 9-13, 9-14, 9-16, 9-17, 9-18, 9-22, 9-23, 9-27, 9-28, 9-35, 9-36, 9-37, 9-39, 9-41, 10-14, 10-28, 11-41, 12-24, 12-35, 12-37, 12-41, 13-17, 13-18, 14-22, 14-28, 14-35, 14-37, 14-41, 16-18, 16-24, 16-35, 16-37, 16-41, 17-18, 17-24, 17-35, 17-37, 17-41, 18-21, 19-22, 19-28, 19-35, 20-22, 20-28, 20-35, 20-37, 20-41,

21, 21-22, 21-28, 21-30, 21-35, 21-37, 21-41, 22, 22-24, 22-28, 22-30, 22-32, 22-35, 22-36, 22-37, 22-38, 22-41, 23-28, 23-35, 23-37, 23-41, 24-28, 24-31, 24-35, 24-36, 24-37, 24-39, 24-41, 25-28, 25-35, 25-37, 25-41, 27, 27-37, 27-38, 27-41, 27-35, 28, 28-30, 28-32, 29-35, 29-37, 30, 30-35, 30-37, 30-41, 31-35, 32-35, 32-37, 32-41, 33-35, 33-37, 33-41, 34-37, 34-41, 35, 35-36, 35-37, 35-41, 37, 37-38, 37-39, 37-40, 37-41, 38-41, 39, 39-41, 41, and 41-42.

4. Rubberlike systems: 89

1-2, 1-2-14, 1-2-21, 1-2-22, 1-2-23, 1-2-24, 1-2-29, 1-2-34, 1-3, 1-5, 1-13, 1-17, 1-22, 1-28, 1-37, 1-41, 2-4, 2-6, 2-13, 2-17, 2-22, 2-24, 2-28, 2-30, 2-32, 2-34, 3-4, 3-9, 3-14, 3-18, 3-19, 3-21, 3-22, 3-23, 3-24, 4-5, 4-28, 4-37, 4-41, 5-9, 6-41, 7-41, 8-37, 8-41, 9-12, 9-13, 9-17, 9-28, 9-37, 9-41, 12-28, 12-37, 12-41, 13-18, 14-22, 14-28, 16-41, 17-18, 17-24, 17-35, 17-41, 20-22, 21, 21-22, 21-28, 21-37, 21-41, 22, 22-24, 22-28, 22-32, 22-41, 24-28, 24-31, 24-41, 27-28, 27-37, 27-41, 28, 28-30, 28-32, 28-35, 30-37, 31-35, 37, 37-39, 37-41, 39-41, and 41.

5. Monomer reactivity ratios determined: 9

System	M_1	M_2	r_1	r_2
1-3	$CF_2{=}CFCl$	Butadiene	0.0	1.35
1-5	$CF_2{=}CFCl$	Isoprene	0.1	1.41
1-2	$CF_2{=}CFCl$	$CF_2{=}CH_2$	0.52	0.17
5-9	$CF_2{=}CCl_2$	Isoprene	0.0	0.45
3-9	$CF_2{=}CCl_2$	Butadiene	0.0	0.80
3-4	$CF_2{=}CF{-}CF{=}CF_2$	Butadiene	0.0	1.35
4-5	$CF_2{=}CF{-}CF{=}CF_2$	Isoprene	0.0	0.75
3-24	$CF_2{=}CF_2$	Butadiene	0.0	1.75
22-24	$CH_2{=}CFCl$	$CF_2{=}CF_2$	2.8	0.1

6. Status of rubberlike systems:

a. Most promising, in pilot plant and undergoing extensive tests: 1-2.

b. Evaluated and rejected as unpromising: 1-3, 1-5, 1-17, 3-9, 5-9, 21, 22 and 28.

c. Promising, to be tested: 1-2-14, 1-2-21, 1-2-22, 1-2-24, 1-2-29, 1-13, 1-22, 1-28, 1-37, 1-41, 2-22, 2-24, 2-30, 2-32, 2-34, 3-4, 3-24, 4-28, 4-37, 4-41, 6-41, 7-41, 8-37, 8-41, 9-13, 9-28, 9-37, 9-41, 12-28, 12-37, 12-41, 16-41, 17-24, 17-35, 17-41, 21-22, 21-37, 21-41, 22-24, 22-41, 24-28, 24-31, 24-41, 27-37, 27-41, 28-32, 28-35, 30-37, 37-39, 37-41, 39-41 and 41.

d. Interesting, but better recipes needed to increase yields or to increase proportion of fluorocarbon combined: 2-4, 2-28, 3-14, 3-18, 3-19, 3-21, 3-23, 14-22, 14-28, 21-28, 22-28, 22-32, 27-28, 28-30, 31-35, and 37.

e. Relatively uninteresting (low F content or negligible amount of third monomer in 1-2-X systems: 1-2-23, 1-2-34, 2-6, 2-13, 2-17, 3-22, 4-5 (isoprene copolymers no longer of interest), 9-12, 9-17, 13-18, 17-18, and 20-22.

II. Summary of Current Progress

During the final period of this contract, the number of monomers available for copolymerization studies has increased to 54, the number of copolymer systems investigated to 357 and the number of rubberlike systems to 145.

Initial results have been received from the screening of a number of raw polymers for oil-resistance and low temperature properties. The indications are that CF_2=CH-C(CH_3)=CH_2 and its copolymers and copolymers of CF_2=CH-CH=CH_2 have fair oil-resistance (25-125% is volume swell in ASTM Reference Fuel No. 2) and reasonably good low temperature properties. The incorporation of a third monomer into the CF_2=CFCl/CF_2=CH_2 (X-300) system fails to improve its low temperature properties or oil-resistance and, in some cases, harms these properties.

The monomers CF_2=C(CH_3)-CH=CH_2 and CF_3-CH=CH-CH=CH_2 have been screened for copolymerizability with many other available monomers. The copolymers obtained, most of them rubbery, have been submitted to the QM Depot as raw polymers to be screened for oil-resistance and low temperature flexibility.

Vinyl butyrate and several vinyl ethers were copolymerized with a number of representative fluoro-olefins. The copolymers with CF_2=CF_2 and CF_2=CF-CF=CF_2 were in nearly all cases rubbery; the CF_2=CF_2 copolymers appeared to be more rubbery. Samples have been sent for screening.

The isocyanate vulcanization of X-300 rubber lacks reproducibility, although strong organic polyamines seem to overcome this difficulty. A number of alternate curing systems are being investigated at Kellogg.

A comparative study of 50/50 and 30/70 molar $CF_2{=}CFCl/CF_2{=}CH_2$ (X-300) copolymers has confirmed earlier indications that the 30/70 product has superior low temperature properties and greater resistance to a variety of swelling agents. QM and Kellogg have agreed to consider shifting the composition at X-300 to the 30/70 molar $CF_2{=}CFCl/CF_2{=}CH_2$ level as soon as practicable.

X-300 has been successfully softened at the QM Depot by the addition of various plasticizers, viscous resins and oils.

Forty-five more pounds of X-300 rubber (50/50) have been shipped to the QM Depot during this period.

III. Experimental Section

A. Monomer Synthesis

Fifty-four monomers are now available for copolymerization studies:

1. $CF_2{=}CFCl$
2. $CF_2{=}CH_2$
3. $CH_2{=}CH{-}CH{=}CH_2$
4. $CF_2{=}CF{-}CF{=}CF_2$
5. $CH_2{=}C(CH_3){-}CH{=}CH_2$
6. $(CH_3)_2C{=}CH_2$
7. $\underbrace{CF_2{-}CF{=}CF{-}CF_2}$
8. $CH_2{=}CHCl$
9. $CF_2{=}CCl_2$
10. $CH_3{-}CH{=}CH_2$
11. $C_6H_5{-}CH{=}CH_2$
12. $CH_2{=}CCl_2$
13. $CH_2{=}CCl{-}CH{=}CH_2$
14. $CF_2{-}CF{=}CF_2$
15. $CF_2{=}CF{-}CN$
16. $CH_2{=}CH{-}CN$
17. $CH_2{=}CH{-}CO_2{-}C_4H_9(n)$

17a. $CH_2{=}CH{-}CO_2{-}CH_3$

18. $CF_2{=}CHCl$
19. $CF_3{-}CCl{=}CCl{-}CF_3$
20. $CF_3{-}C{\equiv}C{-}CF_3$
21. $CF_2{=}CFH$
22. $CH_2{=}CFCl$
23. <u>Cis</u>-$CF_3{-}CH{=}CH{-}CF_3$
24. $CF_2{=}CF_2$
25. <u>trans</u> - $CF_3{-}CH{=}CH{-}CF_3$
26. $CH_2{=}CH{-}C_6H_5{-}CH{=}CH_2$
27. $CH_2{=}C\begin{smallmatrix}CF_3\\CH_3\end{smallmatrix}$
28. $CH_2{=}CF{-}CH{=}CH_2$
29. $CF_2{=}C\begin{smallmatrix}CF_3\\CF_3\end{smallmatrix}$
30. $CF_2{=}CFBr$
31. $CH_2{=}CH_2$
32. $CF_2{=}CCl{-}CF_3$
33. $CF_3{-}C(CH_3){=}CH{-}COOH$
34. $CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}NH_2$
35. $CF_3{-}CH{=}CH_2$
36. $CH_2{=}CHBr$
37. $CF_2{=}CH{-}CH{=}CH_2$
38. $CF_3{-}CCl{=}CCl_2$
39. $CF_3{-}CCl{=}CH_2$
40. $CH_2{=}CHF$
41. $CF_2{=}CH{-}C(CH_3){=}CH_2$
42. $CF_3{-}CH{=}CF_2$
43. $CF_3{-}CH{=}CH{-}CH{=}CH_2$
44. $CF_2{=}C(CH_3){-}CH{=}CH_2$
45. $CH_2{=}CH{-}O{-}CO{-}CH_3$

45a. $CH_2{=}CH{-}O{-}CO{-}CH_2{-}CH_2{-}CH_3$

45b. $CH_2{=}CH{-}O{-}CO{-}CH_2Cl$

46. $C_6H_5{-}CH{=}CH{-}CO_2CH_3$
47. $CH_2{=}CH{-}O{-}CH_2{-}CH_3$
48. $CH_2{=}CH{-}O{-}CH_2{-}CH_2{-}Cl$
49. $CH_2{=}CH{-}O{-}CH_2CH(CH_3)_2$
50. $CF_2{=}C(CH_3){-}CF{=}CH_2$
51. $CF_2{=}CH{-}CF{=}CH_2$
52. <u>trans</u> - $C_2H_5O_2C{-}CH{=}CH{-}CO_2C_2H_5$
53. <u>cis</u> - $C_2H_5O_2C{-}CH{=}CH{-}CO_2C_2H_5$
54. $CH_2{=}CH{-}Si(OC_2H_5)_3$

Dr. Tarrant of the University of Florida prepared two of the twelve new monomers:

#50. $CF_2{=}C(CH_3){-}CF{=}CH_2$ Received as the precursor

$CF_2Br{-}CH(CH_3){-}CFBr{-}CH_3$, 700 g., b.p. 65-66°/29.5 mm.

Preparation:

$$CF_2Br_2 + CH_2{-}CH{=}CF{-}CH_3 \xrightarrow[\text{peroxide}]{\text{benzoyl}} CF_2Br{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CFBr{-}CH_3$$

#51. $CF_2{=}CH{-}CF{=}CH_2$ Received as the precursor

$CF_2Br{-}CH_2{-}CFBr{-}CH_3$, 400 g., b.p. 55-57°/40 mm.

The other new monomers were obtained as samples or by purchase.

No.	Monomer	Source
#45	$CH_2{=}CH{-}O{-}CO{-}CH_3$	Matheson Co.
#45a	$CH_2{=}CH{-}O{-}CO{-}CH_2{-}CH_2{-}CH_3$	Carbon & Carbide Chemicals Corp.
#45b	$CH_2{=}CH{-}O{-}CO{-}CH_2Cl$	Monomer-Polymer, Inc.
#46	$C_6H_5{-}CH{=}CH{-}CO_2CH_3$	Matheson Co.
#47	$CH_2{=}CH{-}O{-}CH_2{-}CH_3$	Matheson Co.
#48	$CH_2{=}CH{-}O{-}CH_2{-}CH_2Cl$	Monomer-Polymer, Inc.
#49	$CH_2{=}CH{-}O{-}CH_2{-}CH(CH_3)_2$	Monomer-Polymer, Inc.
#52	<u>trans</u> - $C_2H_5O_2C{-}CH{=}CH{-}CO_2C_2H_5$	Matheson Co.
#53	<u>Cis</u> - $C_2H_5O_2C{-}CH{=}CH{-}CO_2C_2H_5$	Matheson Co.
#54	$CH_2{=}CH{-}Si(OC_2H_5)_3$	Linde Air Products Co.

Additional supplies of three monomers already on the list were received from Dr. Syverson of The Ohio State University.

No.	Monomer	Amount	B.P.
28.	$CH_2{=}CF{-}CH{=}CH_2$	71 g.	11.3 - 12.0°C.
35.	$CF_3{-}CH{=}CH_2$	ca. 100 g.	
22.	$CH_2{=}CFCl$	10.8 lb.	-27 to -21°C.

Monomers shipped to Bureau of Standards

An additional 10 g. of CF_2=CFBr were sent to Dr. D.E. Mann of the Thermodynamic Section of the National Bureau of Standards for study of its Raman spectrum. Previously, 50 g. of CF_2=CFBr along with several other fluorocarbons, had been sent for a vibrational spectrum study.

B. Monomer Analyses

The following monomers have been analyzed during this period with the mass spectrometer:

a. CF_3-CH=CH-CH=CH_2 Tank No. D-122M-43-1

Approximate analysis:

$C_6H_7F_3$ <0.1%

6 or more H compounds (not $C_6H_7F_3$) - probably small concentrations. Chlorine (cannot identify any chlorine-containing compound from spectrum) - trace

b. CF_2=C(CH_3)-CH=CH_2 Tank No. D-122M-44-1

Approximate analysis:

$C_5H_6F_2$	87%
$C_5H_7F_3$	9%
$C_6F_4H_8$	4%

c. CF_3-CH=CH_2 Tank No. D-122M-35-2

Approximate analysis:

$C_3H_3F_3$	97%
$C_4F_2H_4$	2%
$C_4F_3H_5$	0.3%
Chloro compounds	trace
-C_2H_5 -containing compounds	0.6%

Believed to contain appreciable quantities of isomers of CF_3-CH=CH_2, but this cannot be established.

C. Polymer Preparation

Copolymerizations have now been attempted with 357 systems (where the numbers refer to the monomers listed in section III-A, above):

1-2, 1-2-4, 1-2-8, 1-2-9, 1-2-11, 1-2-14, 1-2-21, 1-2-22, 1-2-23, 1-2-24, 1-2-29, 1-2-30, 1-2-31, 1-2-32, 1-2-35, 1-2-40, 1-2-45, 1-2-45a, 1-2-45b, 1-2-52, 1-2-53, 1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 1-9, 1-12, 1-13, 1-14, 1-16, 1-17, 1-18, 1-19, 1-20, 1-21, 1-22, 1-23, 1-27, 1-28, 1-30, 1-35, 1-36, 1-37, 1-39, 1-40, 1-41, 1-42, 1-43, 1-44, 1-45a, 1-47, 1-48, 1-49, 1-54, 2-3, 2-4, 2-6, 2-8, 2-9, 2-12, 2-13, 2-15, 2-16, 2-17, 2-18, 2-19, 2-21, 2-22, 2-23, 2-24, 2-28, 2-29, 2-30, 2-32, 2-34, 2-35, 2-37, 2-38, 2-39, 2-40, 2-42, 2-43, 2-44, 3-4, 3-7, 3-9, 3-14, 3-18, 3-19, 3-20, 3-21, 3-22, 3-23, 3-24, 3-25, 3-30, 3-32, 3-44, 4, 4-5, 4-6, 4-8, 4-9, 4-10, 4-11, 4-12, 4-14, 4-15, 4-17, 4-19, 4-20, 4-21, 4-22, 4-24, 4-25, 4-27, 4-28, 4-29, 4-32, 4-35, 4-37, 4-39, 4-40, 4-41, 4-42, 4-43, 4-44, 4-45a, 4-47, 4-48, 4-49, 5-9, 5-44, 6-8, 6-9, 6-30, 6-37, 6-41, 7-35, 7-37, 7-41, 7-42, 7-43, 7-44, 8-13, 8-24, 8-35, 8-37, 8-40, 8-41, 8-42, 8-44, 9, 9-12, 9-13, 9-14, 9-16, 9-17, 9-18, 9-22, 9-23, 9-27, 9-28, 9-35, 9-36, 9-37, 9-39, 9-40, 9-41, 9-42, 9-43, 9-44, 9-45a, 9-47, 9-48, 9-49, 10-14, 10-28, 11-41, 11-42, 11-44, 12-24, 12-35, 12-37, 12-40, 12-41, 12-42, 12-44, 13-17, 13-18, 14-22, 14-28, 14-35, 14-37, 14-40, 14-41, 14-42, 14-43, 14-44, 16-18, 16-24, 16-35, 16-37, 16-41, 16-44, 17-18, 17-24, 17-35, 17-37, 17-41, 17-44, 18-21, 19-22, 19-28, 19-35, 20-22, 20-28, 20-35, 20-37, 20-40, 20-41, 20-42, 21, 21-22, 21-28, 21-30, 21-35, 21-37, 21-40, 21-41, 21-42, 21-43, 21-44, 21-45a, 21-47, 21-48, 22, 22-24, 22-28, 22-30, 22-32, 22-35, 22-36, 22-37, 22-38, 22-40, 22-41, 22-42, 22-43, 22-44, 23-28, 23-35, 23-37, 23-40, 23-41, 23-42, 23-44, 24-28, 24-31, 24-35, 24-36, 24-37, 24-39, 24-40, 24-41, 24-42, 24-43, 24-44, 24-45a, 24-47, 24-48, 24-49, 25-28, 25-35, 25-37, 25-40, 25-41, 25-42, 25-44, 27, 27-37, 27-38, 27-41, 27-35, 27-40, 27-42, 27-44, 28, 28-30, 28-32, 29-35, 29-37, 29-40, 29-42, 29-43, 30, 30-35, 30-37, 30-40, 30-41, 30-42, 30-44, 31-35, 31-42, 32-35, 32-37, 32-40, 32-41, 32-42, 32-43, 32-44, 33-35, 33-37, 33-40, 33-41, 33-42, 33-44, 33-37, 34-41, 34-42, 34-44, 35, 35-36, 35-37, 35-40, 35-41, 35-42, 35-43, 35-44, 37, 37-38, 37-39, 37-40, 37-43, 38, 38-40, 38-41, 38-42, 38-44, 39, 39-40, 39-41, 39-42, 39-43, 39-44, 40, 40-42, 41, 41-42, 41-43, 41-44, 42, 42-44, 43 and 43-44.

Of these systems, 145 can be considered rubber-like:

1-2, 1-2-14, 1-2-21, 1-2-22, 1-2-23, 1-2-24, 1-2-29, 1-2-32, 1-2-34, 1-2-40, 1-2-45a, 1-2-45b, 1-3, 1-5, 1-13, 1-17, 1-22, 1-28, 1-37, 1-41, 1-43, 1-44, 1-45a, 1-47, 1-48, 1-49, 2-4, 2-6, 2-13, 2-17, 2-22, 2-24, 2-28, 2-30, 2-32, 2-34, 2-44, 3-4, 3-9, 3-14, 3-18, 3-19, 3-21, 3-22, 3-23, 3-24, 3-44, 4-5, 4-28, 4-37, 4-41, 4-43, 4-44, 4-47, 4-48, 4-49, 5-9, 5-44, 6-41, 7-41, 7-43, 7-44, 8-37, 8-41, 8-44, 9-12, 9-13, 9-17, 9-28, 9-37, 9-41, 9-43, 9-44, 12-28, 12-37, 12-41, 13-18, 14-22, 14-28, 14-43, 14-44, 16-41, 16-44, 17-18, 17-24, 17-35, 17-41, 17-44, 20-22, 21, 21-22, 21-28, 21-41, 21-43, 21-44, 21-45a, 22, 22-24, 22-28, 22-32, 22-41, 22-42, 22-43, 22-44, 23-44, 24-28, 24-37, 24-41, 24-43, 24-44, 24-45a, 24-47, 24-48, 24-49, 27-28, 27-37, 27-41, 27-44, 28, 28-30, 28-32, 28-35, 30-37, 30-44, 31-35, 32-43, 32-44, 33-44, 35-37, 35-40, 35-43, 35-44, 37, 37-38, 37-41, 37-43, 38-44, 39-41, 39-44, 41, 41-43, 41-44, 42-44, 43, and 43-44.

Experimental data relative to the exploratory work carried out during the current period are set forth below:

1. Copolymers of CH_2=CHF

A series of copolymerizations were run with CH_2=CHF to complete the screening of this monomer with all monomers currently available. It was found that CH_2=CF is relatively unreactive, and that only the CF_3-CH=CH_2 copolymer was rubbery (#1112, Table 1). All runs are summarized in Table 1.

2. Copolymers of CF_3-CH=CH-CH=CH_2

Results from the copolymerization screening of CF_3-CH=CH-CH=CH_2 appear in Table 2. A more complete screening was not possible because of the short supply of this monomer. The homopolymer of CF_3-CH=CH-CH=CH_2 is rubbery but not very snappy. The copolymers are also rubber-like.

3. Copolymers of CF_2=C(CH_3)-CH=CH_2

A fairly complete screening of this monomer has been carried out. The results are shown in Table 3. The homopolymer itself is rubbery, as are a number of the copolymers.

Both CF_2=C(CH_3)-CH=CH_2 and CF_3-CH=CH-CH=CH_2 behave like reactive dienes; in copolymerization, they resemble butadiene and isoprene rather than perfluorobutadiene.

The copolymers of CF_3-CH=CH-CH=CH_2 and CF_2=C(CH_3)-CH=CH_2 to be screened for low temperature flexibility and oil resistance are listed in Table 11.

4. Copolymers of CF_3-CH=CF_2

Results from the exploratory copolymerizations of CF_3CH=CF_2 (monomer 42) appear in Table 4. This monomer was disappointingly inert, and no interesting rubbery materials were obtained. The copolymers were either non-rubbery or did not contain appreciable amounts of this comonomer. It had been hoped that this monomer would introduce trifluoromethyl groups into the polymer chain as points of irregularity, thus leading to better low-temperature properties. The trifluoromethyl groups should also reduce the solubility of the polymer. In general the available fluorinated propenes, CF_3=CF=CF_2, CF_3CH=CH_2, and CF_3CH=CF_2 have been unreactive or have not given rubbery products. Of the chlorofluoropropenes, CF_3CCl=CCl_2 and CF_3CCl=CH_2 have proved inert and uninteresting as far as we have explored these systems, but CF_3CCl=CF_2 has formed several copolymers in fair yield, some of which may be interesting as rubbers.

5. Vinyl Ether & Vinyl Ester Copolymers

Results from the exploratory copolymerization of representative fluoroolefins with vinyl ethyl ether, vinyl 2-chloroethyl ether, vinyl isobutyl ether, and vinyl butyrate are summarized in Table 5. It was observed that the copolymer with $CF_2=CF_2$ gave the most rubbery product in each case. Copolymers of perfluorobutadiene were rubbery, but somewhat stiffer and shorter than the $CF_2=CF_2$ copolymer.

The $CF_2=CFCl$ copolymers were very slightly rubbery at room temperature.

No attempt was made to determine in each case whether, and to what degree, side-by-side homopolymerization took place. Generally, vinyl ethers produce only balsam-like, low-molecular weight products with radical catalysts. It has been observed that in bulk copolymerization of vinyl ethers and fluoroolefins that some homopolymerization of the vinyl ether occurs. (R.M. Adams and F.A. Bovey, J. Polymer Sci., 9, 481 (1952)).

The copolymers which were obtained in runs 1333 and 1339, in which a 25/75 $CF_2=CFCl$/vinyl ether charge was used, show a high $CF_2=CFCl$ content. A simple calculation shows these analyses cannot represent the composition of all the copolymer formed since appreciably more $CF_2=CFCl$ would have to be present in the copolymer than was charged. This may point to a lack of homogeneity and possibly some side-by-side homopolymerization.

6. $CF_2=CFCl/CF_2=CH_2/X$ Terpolymers

In an attempt to improve the low temperature properties of the $CF_2=CFCl/CF_2=CH_2$ copolymers designated as X-300 rubber, a series of terpolymerizations has been carried out, wherein the $CF_2=CFCl/CF_2=CH_2$ ratio was to be held as closely as possible to 50/50 molar and the third monomer admitted to the system up to 20 mole per cent of the total. A summary of all terpolymerizations carried out during this period appears in Table 6. Of these, Runs 1297, 1315, 1416, 1278, and 1138 are to be screened for oil resistance and low temperature flexibility (Table 11).

Terpolymerization of vinyl acetate to the extent of 20 mole per cent of the whole product results in the disappearance of the rubberiness characteristic of X-300. (Run 1195, Table 6). If the vinyl acetate combined is dropped to 7 mole per cent, the product is still rubbery, but inferior in this respect to X-300 (Run 1278, Table 6). If vinyl butyrate is terpolymerized, however, the product is still rubbery at 20 mole per cent vinyl butyrate, although not extremely so (Run 1316, Table 6). At 4 mole per cent vinyl butyrate (Run 1315), the product is similar to X-300 as far as apparent rubberiness is concerned.

Vinyl chloride as a third monomer in this system has proved disappointing. Amounts up to 20 mole per cent appear to inhibit polymerization, and at best only powdery materials are obtained.

Based on the evaluation of terpolymers 909, 970, 955, 987, 1088 and 1190 where X of system CF_2=CFCl/CF_2=CH_2/X is CH_2=CFCl, CH_2=CFCl, CF_2=CFBr, CH_2=CH_2, CH_2=CHF or CF_2=CHF respectively, (see Table 10 and Figure 3); this approach to improved low temperature properties for X-300 rubbers has been unrewarding. The terpolymers tested have been no better and in some cases poorer than X-300.

Consequently, CF_2=CFCl/CF_2=CH_2/X terpolymerization is being abandoned for the present, and efforts concentrated on arriving at this optimum CF_2=CFCl/CF_2=CH_2 ratio for low temperature flexibility, oil-resistance, and processibility.

7. Reactivity Ratios for the CF_2=CF_2/CH_2=CFCl System

This system is of importance not only because some of its ratios are rubbery, but because it may provide an alternate route to the manufacture of X-300 rubber. A 50/50 molar copolymer of each system contains the same -CF_2-, -CH_2- and -CFCl- groups in the same proportions. Differences should arise only through the arrangement of these groups, i.e., through the mode of addition of the monomer units to each other during copolymerization. As yet, there is no definitive evidence on this point.

Monomer reactivity ratios have been computed for CH_2=CFCl (M_1) and CF_2=CF_2(M_2). The parameters found (r_1= 2.8 ± 0.3, r_2 = 0.1 ± 0.1) are based on the following data:

Run No.	Moles Charged CH_2=CFCl/	Moles Found CF_2=CF_2	% Conversion	Hours /1/ Polymerization	Appearance
689	50/50	82/18	54	24	rubber
809	30/70	26/74	98	78	"
810	10/90	9/91	96	78	powder
1117	50/50	51/49	97	23	"
1118	30/70	32/68	99	23	rubber
1119	30/70	28/72	92	23	powder
1120	10/90	32/68	20	2.5	rubber
1206	50/50	80/20	8	0.3	"
1207	70/30	87/13	12	0.3	"
1208	30/70	67/33	10	0.3	"

/1/ Persulfate-bisulfite-iron suspension recipe at 20°C.

The instantaneous composition diagram for this system is presented in Figure 1. The reactivity parameters show that the radical $-CF_2CF_2\cdot$ prefers M_1 ($CH_2=CFCl$), whereas the radical $-CH_2-CFCl\cdot$ is not as selective, preferring to homopolymerize very slightly. In order to maintain homogeneity in such a system the conversions must be kept very low as the $CH_2=CFCl$ disappears rapidly (cf. Figure 2).

Several $CF_2=CF_2/CH_2=CFCl$ copolymers have been submitted for low temperature flexibility and oil resistance screening tests (Table 11).

8. Miscellaneous Exploratory Copolymerizations

A number of miscellaneous exploratory copolymerizations are summarized in Table 7. Only two of these produced rubbery materials (Runs 1203 and 1277).

Run 1277 yielded a rubbery copolymer of $CF_2=CF_2$ and n-butyl acrylate, presumably of the grafted type. A sample of the raw polymer has been sent for evaluation (Table 11). The corresponding $CF_2=CFCl$ copolymers have not been outstanding in oil resistance and have been difficult to vulcanize. (Progress Report RL-53-259, p. 16).

Run 1203 is the designation of a rubbery material found in a tank in which $CF_2=CF-CF=CF_2$ distillation "tails" had been stored at dry-ice temperature for about three months.

Analysis indicates this material is not polyperfluorobutadiene, and no alternative structure has as yet been assigned.

An attempt to polymerize $CF_2=CF-CF=CF_2$ using azobisisobutyronitrile at 40-60° was a failure, again emphasizing the unreactivity of this monomer (Run 1219). Perfluorobutadiene could not be induced to copolymerize with SO_2 at 60° (Run 1300).

The system $CF_2=CFCl/CH=CH-Si(OC_2H_5)_3$ was unreactive (Run 1236).

9. Extreme Pressure Polymerization

The necessary equipment for running high pressure (10,000 atm) polymerizations has been received from J. Unertl Co., Pittsburgh, Pa. This unit consists of a heavy-walled cylinder and plunger in which a few grams of monomer will be subjected to extreme hydraulic pressures by concentrating the force applied to a large ram on the small diameter plunger. The first experiments will be carried out with $CF_2=CF-CF=CF_2$ in an effort to duplicate W.T. Miller's early work.

10. Polymerization Recipes

For reference purposes the recipes commonly used by the Arctic Rubber Group in exploratory polymerization work are included in this report.

1. Mutual Recipe
Temperature 50°C.

Water	200 parts by weight
Monomers	100 " "
KORR Soap	5 " "
$K_2S_2O_8$	0.3 " "
DDM	0.3 " "
pH	10.2 " "

KORR is the designation for a saturated fatty acid potassium soap supplied in flake form by Proctor and Gamble.

DDM is tertiary dodecyl mercaptan sold by Phillips Petroleum Company.

2. Mutual-F Recipe
Temperature 50°C.

Water	180 parts by weight
Monomers	100 " "
$C_7F_{15}COONH_4$	2.5 " "
$K_2S_2O_8$	0.3 " "
DDM	0.15 " "
pH	10
Concentrated buffer sol.	-20

3. Cumene Hydroperoxide Redox Recipe
(CHP - Redox)
Temperature 20°C.

Water	200 parts by weight
Monomers	100 " "
KORR Soap	5 " "
CHP (100%)	0.15 " "
$Na_4P_2O_7 \cdot H_2O$	1.00 " "
$FeSO_4 \cdot 7H_2O$	0.10 " "
Dextrose	1.00 " "
DDM	0.3 " "

CHP is supplied by Hercules as a 75% solution.

4. Persulfate-Bisulfite-Iron Suspension Recipe
Temperature 20°C.

Water	200 parts by weight
Monomers	100 " "
$(NH_4)_2S_2O_8)$	1.0 " "
$Na_2S_2O_5$	0.4 " "
$FeSO_4 \cdot 7H_2O$	0.1 " "

The parts by weight of catalysts are frequently varied. The above recipe is typical.

5. Mass Polymerization Recipe
Temperature -15°C.

Monomers	100 parts by weight
Bis-trichloroacetyl peroxide	0.037 " "
Freon-11	<0.93 " "

The catalyst is handled in Freon-11 solution. Some of this solvent is cautiously evaporated before adding monomers. The amount of catalyst is only illustrative; it may be varied considerably.

D. Polymer Evaluation

1. Properties and Uses of X-300 Rubber

a. Vulcanization

It was found during this period that the high tensile strength formerly obtained from the diisocyanate vulcanization of X-300 rubber could not be duplicated. However, it has since been shown that the diisocyanate cure can be accelerated with strongly basic organic amines such as triethylene tetramine (TETA). These latest findings are summarized in Tables 8 and 9. The addition of the amine to the MDI/ZnO recipe increases the tensile strength from 700 psi to >1500 psi. Both TETA and hexamethylene tetramine (HMTA) have been used successfully. None of the curing agents synthesized at Kellogg appears to be superior to MDI.

Strongly basic organic diamines (alone) can also bring about X-300 vulcanization, as illustrated by the high tensiles observed for stock 13F48. However, high levels of amines (e.g., 5 parts per 100 parts of X-300) tend to scorch the rubber during milling and to prevent easy flow during molding.

An intensive search for curing agents other than isocyanates and amines is being carried out at Kellogg. The results of this study will be reported when more data are available.

b. Softeners & Fillers

An increase in the plasticity of X-300 is highly desirable, especially for stocks which are to be calendered or extruded.

The QM Depot has attempted to soften X-300 rubber by incorporating plasticizers, viscous resins and oils. Such additives as over-modified X-300, telomer broad cut, Flexol TOF, Reogen, Vistanex B-100, dibutyl sebacate and Mercoflex 600 have been used in quantities up to 20 parts per 100 parts of X-300 to produce smooth sheets with the X-300/ZnO/MDI/TETA (100/5/5/1) recipe. The softening of X-300 stock by other means, such as changes in copolymer ratio (50/50 to 30/70) and molecular weight modification during polymerization is also being considered.

c. End Items for QM

Protective suits, boots, and gloves are the end items of greatest interest to QM. Work has been delayed on these applications for X-300 rubber because of difficulties encountered in reproducing the isocyanate cure. However, some of the newer curing systems look promising enough for end item development to be resumed during the next period.

2. Screening of Raw Polymers

In an attempt to evaluate rapidly the large number of copolymers prepared in our exploratory work, it was decided after consultation with Mr. Griffis of the QM Depot, that small unvulcanized samples of each copolymer should be subjected to the Gehman stiffness and volume swell test (see previous progress report, RL-53-274, p.16). It is hoped that this procedure will enable us to arrive at a useful comparison of the low temperature and oil-resistance properties of all rubbery materials prepared to date in a minimum of time.

It is difficult to predict how reliable a comparison of this type will be, based as it is on raw polymers and not on the final, cured and compounded rubber. However, it appears to be a realistic approach and should serve as a guide to future work.

The results of the screening tests on the initial lots of rubbery polymers have been received (cf. Table 10). In the table are listed all rubbery systems prepared up to the end of this period and their status with regard to evaluation, primarily from the point of view of raw polymer properties. Copolymers tested as vulcanizates are not treated in detail in this table. Monomers are referred to in Table 10 by their code numbers;

these are identified at the foot of the table. The Gehman stiffness data are expressed in terms of T_2, T_5, T_{10} and T_{100} temperatures, i.e., the temperatures at which the specimen is 2, 5, 10 and 100 times stiffer than at 25°C. The per cent volume increase was determined in ASTM Reference Fuel No. 2, which consists of isooctane (60% by vol.), benzene (5%), toluene (20%) and xylene (15%). These swelling values are subject to some error because of the small samples used. The Gehman test samples were molded from raw polymer. The right hand columns in Table 10 give the molding temperature and appearance of the raw polymers after molding.

Many rubbery systems are labeled "no test" in Table 10. This generally means that the samples available were judged unsatisfactory or were not deemed interesting enough on inspection to warrant further screening.

Some preliminary conclusions from the screening tests:

a. Copolymers of CF_2=CH-CH=CH_2 and CF_2=CH-C(CH_3)=CH_2) seem to have surprisingly good oil resistance. Compare Figures 4, 5 and 6. In addition, it appears that CF_2=CH-CH=CH_2 copolymers are more oil resistant than those of CF_2=CH-C(CH_3)=CH_2.

b. Few data are available for comparison of the low-temperature properties of the 1,1-difluorodiene copolymers with butadiene copolymers. Runs 515 and 1013 (Figures 4 and 5) suggest that the butadiene copolymer of CF_2=CF-CF=CF_2 is more flexible than the copolymer of CF_2=CH-CH=CH_2 with CF_2=CF-CF=CF_2. However, the CF_2=CF_2 copolymers of the three dienes (Runs 573, 1129 and 1130) at approximately the same CF_2=CF_2 level have very similar low-temperature properties.

c. The screening test revealed that the Gehman stiffness of a 35/65 CF_2=CH_2/CF_2=CF_2 copolymer changes very little as the temperature decreases. (See Run 572, Table 10, and Figure 3.) Unfortunately, this copolymer is virtually non-rubberlike at room temperature. An attempt will be made, however, to determine whether other ratios are rubbery and whether the introduction of a third monomer such as CF_2=CFCl will produce a rubbery product.

d. Raw polymer samples of X-300 and X-300, 30/70 ratio, have been screened as reference points (Figure 3). Hycar OR-15, a commercially available oil resistant rubber, is also included for reference. X-300 containing 70 mole % CH_2=CF_2 is somewhat superior to Hycar OR in both oil resistance and low temperature properties.

e. X-300 is still not the answer to the Arctic Rubber problem, despite its apparent utility in other applications (e.g., for acid resistance). During the next contract year, commencing Aug. 1, 1953, emphasis will be placed on further screening of exploratory polymers and on the polymerization of unreactive monomers (e.g., CF_3-CF=CF_2) by unusual means (e.g., extreme pressure, see below).

3. Raw Polymers Shipped for Screening during this Period

The products described in Table 11 were shipped to the QM Depot for evaluation during the current period.

IV. Pilot Plant Production of X-300 Rubber

During this period, 45 lb. of X-300 were made for the QM account and shipped to the Philadelphia Depot.

V. Final Report - Plans for Future Work under New Contract

A final report covering all work done under DA-44-109-qm-222 from July 1, 1950 through July 31, 1953 is being prepared.

A new contract, with the same objectives as the old, is being negotiated with QM. Under this new contract, the plans for future work will include:

1. Pilot plant production of X-300 for thorough evaluation in a variety of end items (of immediate interest: protective suits, hoods, gloves, and boots).

2. Filler, Softener, Vulcanization studies on X-300.

3. Improved X-300 polymer.

4. Screening the more promising rubbers noted in the "past progress" section by means of Gehman stiffness and volume swell measurements on pressed sheets of the raw polymers.

5. Exploratory polymerization of new monomer pairs and development of better recipes where needed to improve yields,

6. High pressure polymerization of unreactive fluoro-olefins.

J. M. Hoyt
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F. J. HONN

J. W. Copenhaver
J. W. COPENHAVER

Reference to Original Records

Notebook #135 (A.N. Bolstad), p. 188-199, incl.

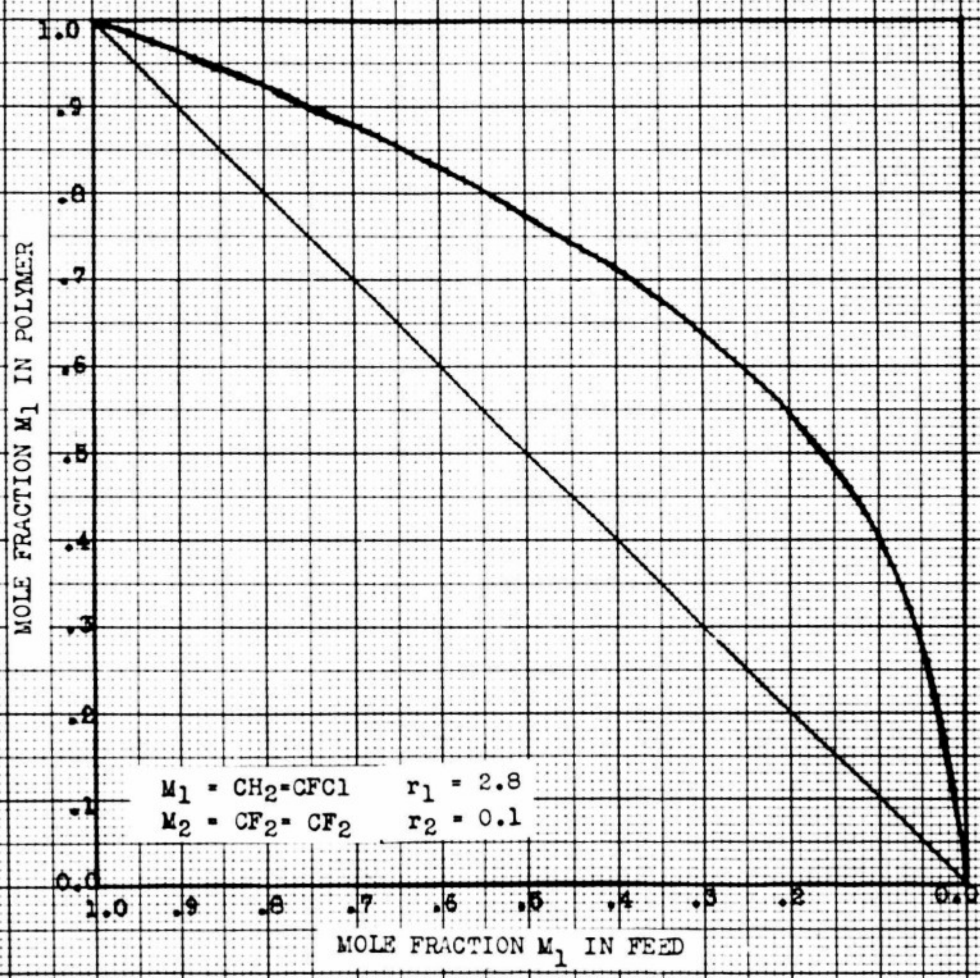
Notebook #234 (A.N. Bolstad), p. 1-53, incl.

Notebook #202 (F.N. Roberts), p. 159

Notebook #226 (J.M. Hoyt), p. 1-112 incl.

FIGURE 1

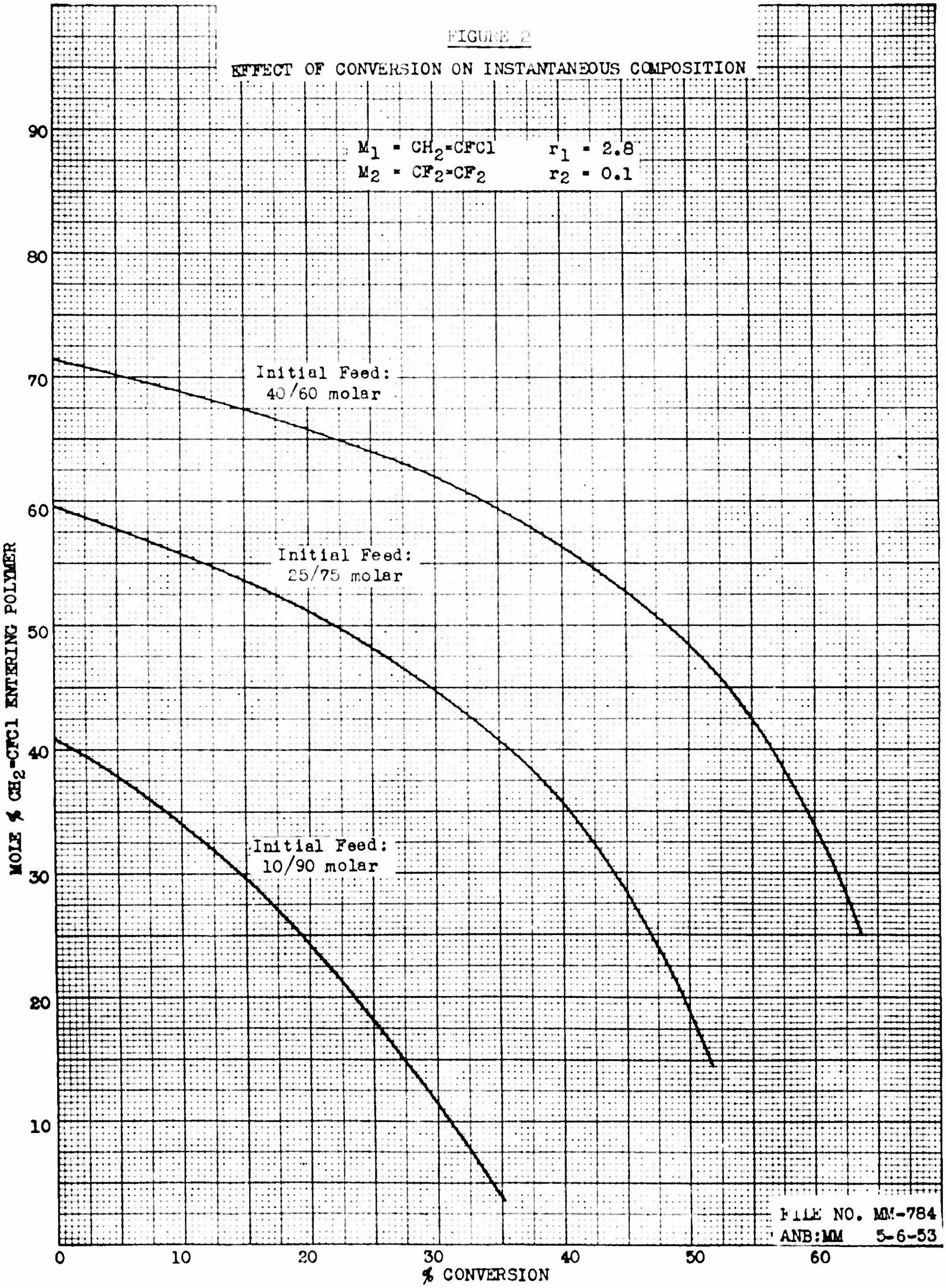
INSTANTANEOUS POLYMER/FEED COMPOSITION DIAGRAM



FILE NO. MM-783
ANB:MM 5-6-53

FIGURE 2

EFFECT OF CONVERSION ON INSTANTANEOUS COMPOSITION



FILE NO. MM-784
ANB:MM 5-6-53

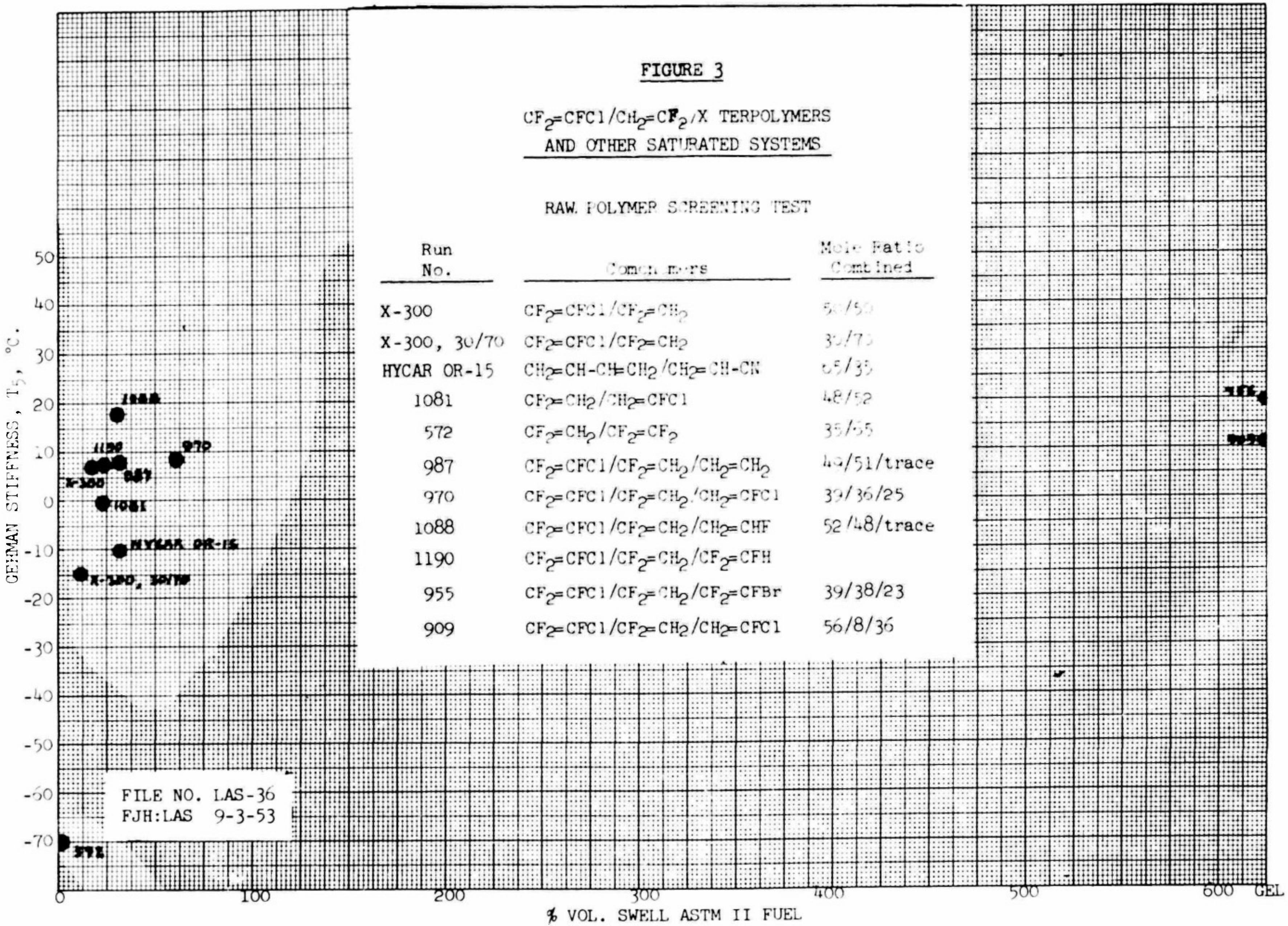


FIGURE 3

$CF_2=CFCl/CH_2=CF_2/X$ TERPOLYMERS AND OTHER SATURATED SYSTEMS

RAW POLYMER SCREENING TEST

Run No.	Comonomers	Mole Ratio Combined
X-300	$CF_2=CFCl/CF_2=CH_2$	50/50
X-300, 30/70	$CF_2=CFCl/CF_2=CH_2$	30/70
HYCAR OR-15	$CH_2=CH-CH=CH_2/CH_2=CH-CN$	65/35
1081	$CF_2=CH_2/CH_2=CFCl$	48/52
572	$CF_2=CH_2/CF_2=CF_2$	35/65
987	$CF_2=CFCl/CF_2=CH_2/CH_2=CH_2$	49/51/trace
970	$CF_2=CFCl/CF_2=CH_2/CH_2=CFCl$	39/36/25
1088	$CF_2=CFCl/CF_2=CH_2/CH_2=CHF$	52/48/trace
1190	$CF_2=CFCl/CF_2=CH_2/CF_2=CFH$	
955	$CF_2=CFCl/CF_2=CH_2/CF_2=CFBr$	39/38/23
909	$CF_2=CFCl/CF_2=CH_2/CH_2=CFCl$	56/8/36

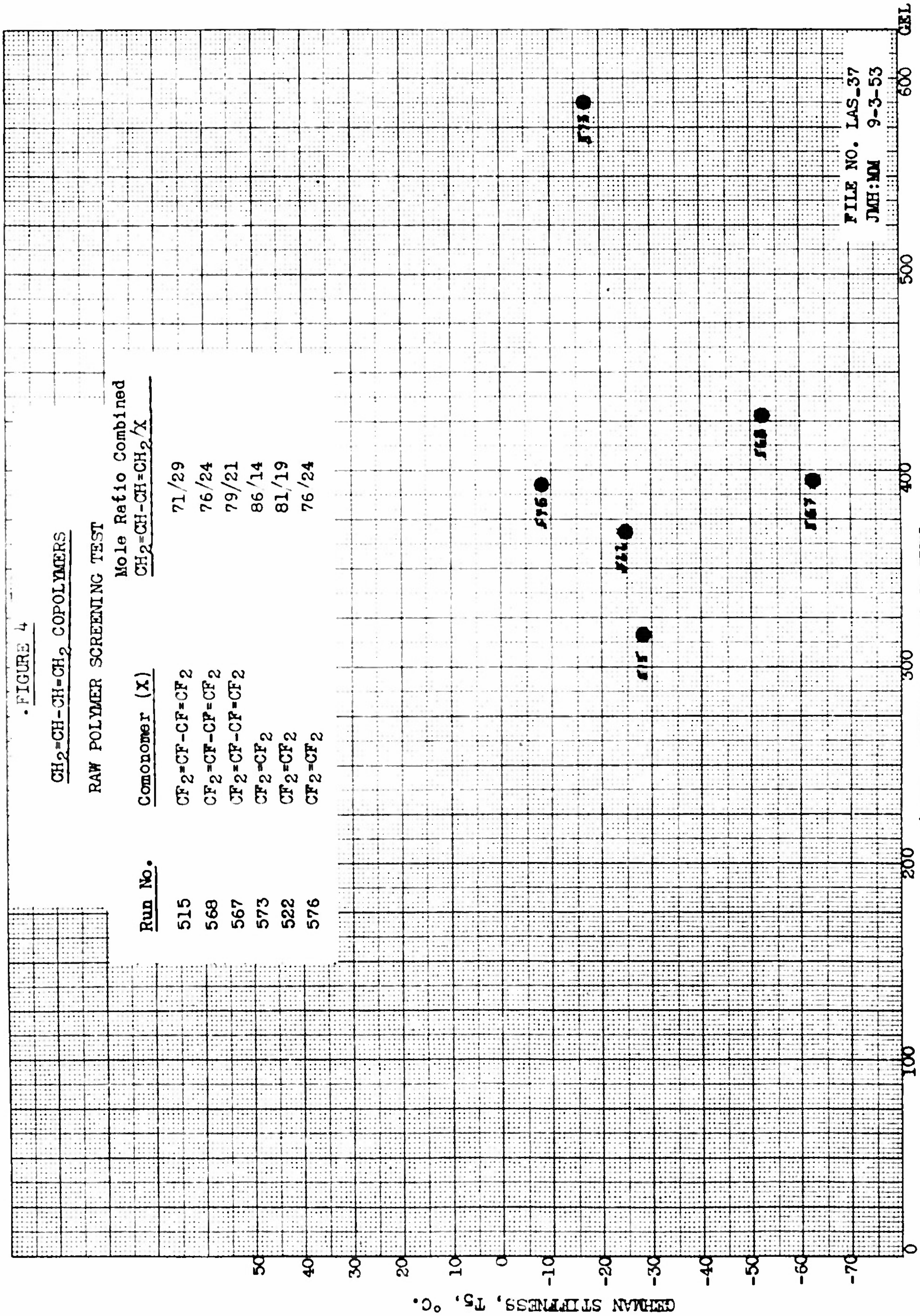
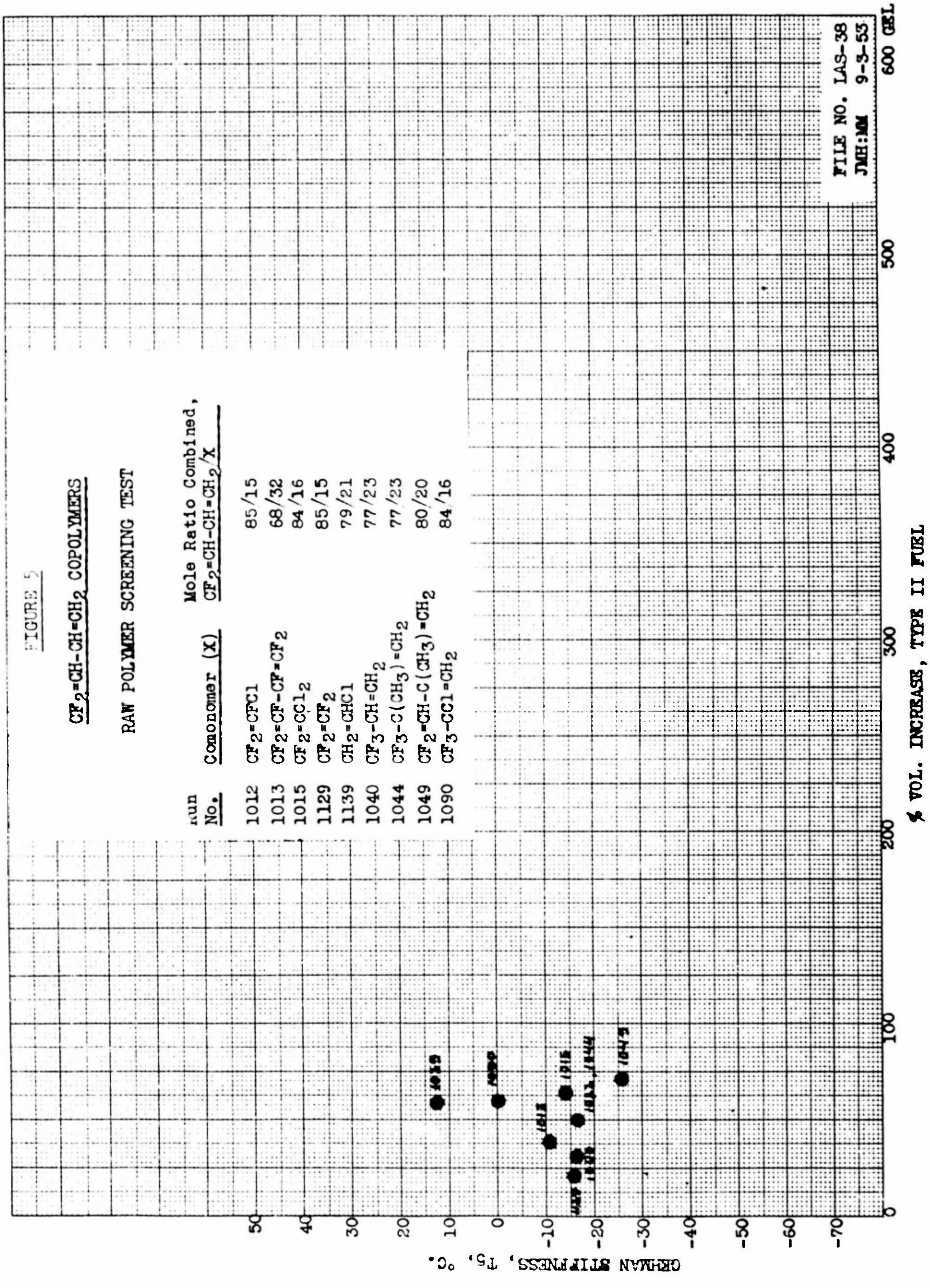


FIGURE 4
CH_2=CH-CH=CH_2 COPOLYMERS
RAW POLYMER SCREENING TEST
Run No. | Comonomer (X) | Mole Ratio Combined CH_2=CH-CH=CH_2/X
515 | CF_2=CF-CF=CF_2 | 71/29
568 | CF_2=CF-CF=CF_2 | 76/24
567 | CF_2=CF-CF=CF_2 | 79/21
573 | CF_2=CF_2 | 86/14
522 | CF_2=CF_2 | 81/19
576 | CF_2=CF_2 | 76/24
573
568
576
567
522
515
FILE NO. LAS-37
JMH:MM 9-3-53
0
100
200
300
400
500
600
GEL
% VOL. INCREASE, TYPE II FUEL
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
GEHMAN STIFFNESS, T5, °C.

THE M. W. KELLOGG COMPANY
Petroleum & Chemical
Research Dept.
Jersey City, N. J.

Report No. RL-53-289

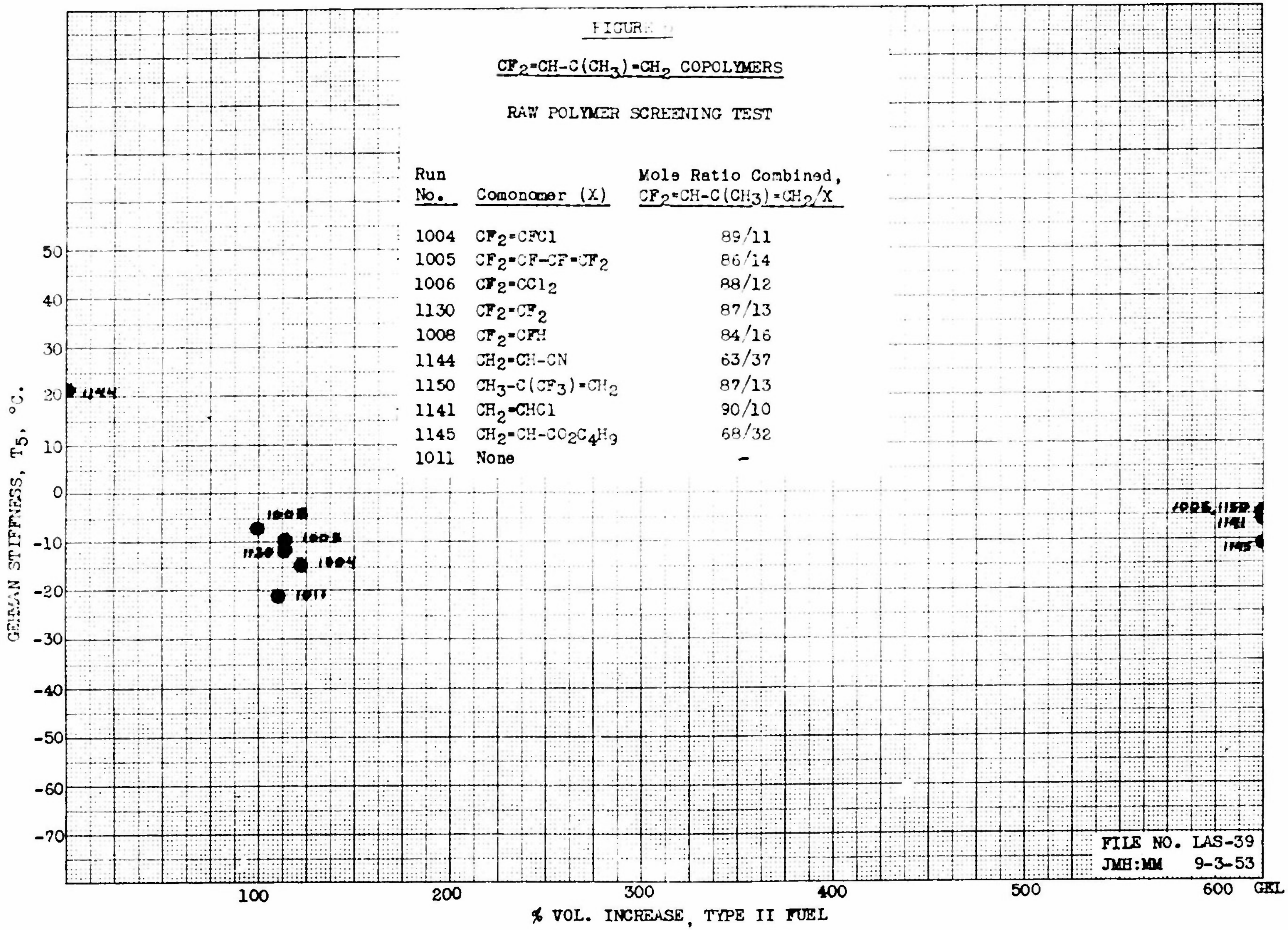


FIGURE

$CF_2=CH-C(CH_3)=CH_2$ COPOLYMERS

RAW POLYMER SCREENING TEST

Run No.	Comonomer (X)	Mole Ratio Combined, $CF_2=CH-C(CH_3)=CH_2/X$
1004	$CF_2=CFCl$	89/11
1005	$CF_2=CF-CF=CF_2$	86/14
1006	$CF_2=CCl_2$	88/12
1130	$CF_2=CF_2$	87/13
1008	$CF_2=CFH$	84/16
1144	$CH_2=CH-CN$	63/37
1150	$CH_3-C(CF_3)=CH_2$	87/13
1141	$CH_2=CHCl$	90/10
1145	$CH_2=CH-CO_2C_4H_9$	68/32
1011	None	-



FILE NO. LAS-39
JMH:MM 9-3-53

TABLE 1

$CH_2=CHF$ COPOLYMERIZATIONS

Recipe: Persulfate-bisulfite suspension, 23 hr., 20°C.
Molar Charge Ratio: 50/50

Run No.	Comonomer (X)	% Conversion	Moles $CH_2=CHF/X$ Combined	Appearance
1093	$CF_2=CFCl$	96	53/47	powder
1094	$CF_2=CH_2$	trace	-	-
1095	$CF_2=CFCF=CF_2$	zero	-	-
1096	$CF_2CF=CFCF_2$	trace	-	-
1097	$CH_2=CHCl$	16	8/92	white solid
1098	$CF_2=CCl_2$	4	60/40	powder
1099	$CH_2=CCl_2$	25	12/88	powder
1100	$CF_3CF=CF_2$	40	71/29	crumbly solid
1101	$CF_3C\equiv CCF_3$	zero	-	-
1102	$CF_2=CHF$	2	0/100	powder
1103	$CH_2=CFCl$	87	44/56	powder sl. rubbery
1104	$CF_3CH=CHCF_3$(cis)	trace	-	-
1105	$CF_2=CF_2$	5	64/36	powder
1106	$CF_3CH=CHCF_3$(trans)	zero	-	-
1107	$CH_3C(CF_3)=CH_2$	zero	-	-
1108	$(CF_3)_2C=CF_2$	zero	-	-
1109	$CF_2=CFBr$	12	55/45	crumbly solid
1110	$CF_3CCl=CF_2$	21	58/42	papery solid
1111	$CH_3C(CF_3)=CHCOOH$	trace	-	-
1112	$CH_2=CHCF_3$	2	29/71	hard, tough rubber
1113	$CF_3CCl=CCl_2$	zero	-	-
1114	$CF_3CCl=CH_2$	zero	-	-
1115	none	trace	-	-
1116	$CF_3CH=CF_2$	zero	-	-

FILE NO. LAS-106
FJH:SB 1/7/54

TABLE 2

CF_3-CH=CH-CH=CH_2 COPOLYMERIZATIONS

Recipe: Mutual-F, 90 hours, 50°C. /1/
Molar Charge Ratio: 50/50

No.	Comonomer-(X)	% Conversion	Moles CF_3-CH=CH-CH=CH_2/X Combined	Appearance
1243	CF_2=CF-CF=CF_2	41	82/18	stiff rubber
1244	CF_2=CCl_2	38	89/11	slow rubber
1245	CF_3-CF=CF_2	42	79/21	stiff rubber
1246	CH_2=CFCl	51	81/19	slow rubber
1247	$(CF_3)_2C$=CF_2	0	-	-
1248	CF_3-CCl=CF_2	36	95/5	stiff rubber
1249	CF_2=CH-C(CH_3)=CH_2	92 /2/	90/10	rubber
1250	CF_3-CCl=CH_2	trace	-	-
1251	CF_2=CH-CH=CH_2	100 /2/	90/10	rubber
1252	CF_3-CH=CH_2	40	86/14	stiff rubber
1253	none	94 /2/	100/0	rubber
1254	CF_2=C(CH_3)-CH=CH_2	80 /2/	97/3	rubber
1255	CF_2-CF=CF-CF_2 (ring)	10	96/6	rubber

Recipe: CHP - Redox, 24 hours, 20°C. /1/
Molar Charge Ratio: 48/52

No.	Comonomer-(X)	% Conversion	Moles CF_3-CH=CH-CH=CH_2/X Combined	Appearance
1215	CF_2=CH_2	trace	-	-
1216	CF_2=CF_2	48	86/14	slow rubber
1217	CF_2CFH	24	/4/	slow rubber
1218	CF_2=CFCl /3/	37	99/1	fast rubber

/1/ See section on recipes elsewhere in this report.
/2/ Polymerization time 24 hours.
/3/ Molar ratio 50/50
/4/ Fluorine content too low for either homopolymer; product probably loses HF.

FILE NO. LAS-109
FJH:SB 1/7/54

TABLE 3

COPOLYMERS OF $CF_2=C(CH_3)-CH=CH_2$

Recipe: Mutual, 24 hours, 50°C. /1/
Molar Charge Ratio: 50/50

No.	Comonomer	% Conversion	Moles $CF_2=C(CH_3)-CH=CH_2$/X Combined	Appearance
1221	$CF_2=CFCl$	54	75/25	rubber
1222	$CH_2=CH-CH=CH_2$	83	48/52	soft rubber
1225	$CH_3-C(CF_3)=CH_2$	33	91/9	rubber
1226	$CH_2=CHCl$	49	82/18	soft rubber
1227	$CH_2=C(CH_3)-CH=CH_2$	86	50/50	slightly tacky rubber
1228	$CH_2=CCl_2$	1	-	soft, sticky rubber
1229	$CH_2=CH-CN$	79	88/12	stiff rubber
1230	$CF_3-CCl=CF_2$	23	97/3	soft rubber
1231	$CF_3-CH=CH_2$	38	99/1	soft rubber
1232	$CF_3-CCl=CH_2$	35	81/19	slow rubber
1233	$CF_2=CH-C(CH_3)=CH_2$	94	-	rubber
1234	$CF_3-CH=CF_2$	32	82/18	soft rubber
1237	$CF_3-CCl=CCl_2$	40 /1/	96/4	soft, weak rubber
1238	$CH_2=CH-C(=O)-NH_2$	96 /1/	80/20 /2/	hard, bluish-white resin
1239	$CH_2=CFCl$	55 /1/	93/7	rubber
1240	$N-CH_2=CH-C(=O)-OC_4H_9$	91 /1/	52/48	soft, slightly tacky rubber
1241	$CF_2=CFBr$	15 /1/	96/4	soft, slightly tacky rubber
1242	Styrene	92 /1/	64/36	paper-like solid
1272	$CF_2=CF-CF=CF_2$	29	88/12	slow rubber
1273	$CF_2=CCl_2$	50	78/22	rubber
1289	cis-$CF_3-CH=CH-CF_3$	20	99/1	slightly tacky rubber
1290	$CH_3-C(CF_3)=CH-COOH$	0.2	-	rubber
1291	$CF_3-CF=CF_2$	22	98/2	slow rubber
1292	trans-$CF_3-CH=CH-CF_3$	17	trace F only	slow rubber
1293	$CF_2-CF=CF-CF_2$ (ring)	16	99/1	slow rubber

/1/ Run length 40 hours.
/2/ May indicate that product is not homogeneous.

Recipe: CHP Redox, 24 hours, 20°C.

No.	Comonomer-(X)	% Conversion	Moles $CF_2=C(CH_3)-CH=CH_2$/X Combined	Appearance
1211	$CH_2=CF_2$	38	90/10	rubber
1212	$CF_2=CF_2$	49	90/10	rubber
1213	$CF_2=CFH$	49	90/10	rubber

FILE NO. LAS-108
FJH:SB 1/7/54

TABLE 4

CF_3-CH=CF_2 COPOLYMERIZATIONS

Recipe: Persulfate-Bisulfite-Iron Suspension, 20°C., 24 hours
Molar Charge Ratio: 50/50

No.	Comonomer (X)	Moles $CF_3CH=CF_2$/X Combined	% Conversion	Appearance
1161	$CF_2=CFCl$	2/98	28	Powder
1162	$CF_2=CH_2$	-	blew up	-
1163	$CF_2=CFCF=CF_2$	-	zero	-
1164	$CF_2CF=CFCF_2$	-	zero	-
1165	$CH_2=CHCl$	0/100	22	Powder
1166	$CF_2=CCl_2$	-	zero	-
1167	$C_6H_5CH=CH_2$	-	trace	-
1168	$CH_2=CCl_2$	0/100	6	Hard particles
1169	$CF_3CF=CF_2$	-	zero	-
1170	$CF_3C\equiv CCF_3$	-	zero	-
1171	$CF_2=CHF$	-	blew up	-
1172	$CH_2=CFCl$	3/97	11	Rubber
1173	(cis)$CF_3CH=CHCF_3$	-	zero	-
1174	$CF_2=CF_2$	F too low for either monomer	40	Powder
1175	(trans)$CF_3CH=CHCF_3$	-	zero	-
1176	$CH_3C(CF_3)=CH_2$	-	zero	-
1177	$(CF_3)_2C=CF_2$		zero	-
1178	$CF_2=CFBr$	2/98	10	White solid
1179	$CH_2=CH_2$	-	blew up	-
1180	$CF_3CCl=CF_2$	-	zero	-
1181	$CH_3C(CF_3)=CHCOOH$	-	zero	-
1182	$CF_3CH=CH_2$	-	zero	-
1183	$CF_3CCl=CCl_2$	-	zero	-
1184	$CH_2=CHC(=O)-NH_2$	--------- Some water soluble polymer - not isolated ---------		
1185	$CF_3CCl=CH_2$	-	zero	-
1186	None	-	zero	-

FILE NO. MM-859
JMH:MM 9-3-53

TABLE 5

VINYL ETHER & VINYL ESTER - FLUOROOLEFIN COPOLYMERS

Vinyl Ethyl Ether (VEE) Copolymers

Recipe (parts by wt.): Water 180; Monomers 100; KORR soap 5.0; $K_2S_2O_8$ 0.3; conc. buffer soln. 20; pH = 10.0; Temp. = 50°C.

No.	Comonomer (X)	Moles VEE/X Charged	Moles VEE/X Combined	% Conversion	Hrs. Polymer-ization	Appearance
1331	$CF_2=CFCl$	50/50	49/51	89	2	Tough, very slightly rubbery
1332	$CF_2=CFCl$	25/75	44/56	50	22	Hard, inelastic
1333	$CF_2=CFCl$	75/25	33/67	57	2	Brittle, very slightly rubbery
1334	$CF_2=CF-CF=CF_2$	50/50	47/53	89	22	/1/
1335	$CF_2=CCl_2$	50/50	38/62	32	2	Brittle
1336	$CF_2=CFH$	50/50	-	trace	22	-
1348	$CF_2=CF_2$	50/50	52/48	41	4	Soft, rubbery crumb

Vinyl 2-Chloroethyl Ether (VCEE) Copolymers

Recipe (parts by wt.): Water 200; Monomers 100; KORR soap 5.0; $K_2S_2O_8$ 0.3; conc. buffer soln. 20; pH = 10.0; Temp. = 50°C.

No.	Comonomer (X)	Moles VCEE/X Charged	Moles VCEE/X Combined	% Conversion	Hrs. Polymer-ization	Appearance
1337	$CF_2=CFCl$	25/75	44/56	45	4	Tough, inelastic
1338	$CF_2=CFCl$	50/50	48/52	71	3	Tough, inelastic
1339	$CF_2=CFCl$	75/25	40/60	52	3	Hard, slow rubber
1340	$CF_2=CF_2$	50/50	51/49	40	2	Rubber
1341	$CF_2=CF-CF=CF_2$	50/50	86/14	50	5	Rubber
1342	$CF_2=CCl_2$	50/50	45/55	23	5	Brittle
1343	$CF_2=CFH$	50/50	-	1	5	Short, slow rubber

Vinyl Isobutyl Ether (VIE) Copolymers

Recipe (parts by wt.): Water 180; Monomers 100; KORR soap 4.5; $K_2S_2O_8$ 0.3; conc. buffer soln. 16.4; pH = 10.2. Temperature = 50°C.

No.	Comonomer (X)	Moles VIE/X Charged	Moles VIE/X Combined	% Conversion	Hr. Polymer-ization	Appearance
1301	$CF_2=CFCl$	75/25	48/52	52	1 1/4	hard, very slightly rubbery
1302	$CF_2=CFCl$	50/50	47/53	78	1 1/4	hard, very slightly rubbery
1307	$CF_2=CFCl$	25/75	45/55	37	1 1/3	hard, very slightly rubbery
1304	$CF_2=CF_2$	50/50	48/52	41	1 1/4	rubber
1305	$CF_2=CCl_2$	50/50	56/44	9	1 1/4	hard, very slightly rubbery
1306	$CF_2=CF-CF=CF_2$	50/50	48/52	96	18	short rubber.

Vinyl Butyrate (VB) Copolymers

Recipe (parts by wt.): Water 200; Monomers 100; KORR soap 5.0; $K_2S_2O_8$ 0.3; conc. buffer soln. 20; pH = 10.0; Temp. = 50°C.

No.	Comonomer (X)	Moles VB/X Charged	Moles VB/X Combined	% Conversion	Hr. Polymer-ization	Appearance
1317	$CF_2=CF_2$	50/50	65/35	16	1/3	Rubber
1318	$CF_2=CFCl$	75/25	70/30	14	1/3	Soft, slow rubber
1319	$CF_2=CFCl$	50/50	55/45	34	1/3	Hard, slightly rubbery
1320	$CF_2=CFCl$	25/75	45/55	46	1/3	Hard, slightly rubbery
1323	$CF_2=CF-CF=CF_2$	50/50	-	15	26	Brittle
1324	$CF_2=CCl_2$	50/50	28/72	23	2-1/2	Paper-like, transparent
1325	$CF_2=CFH$	50/50	75/25	6	1-1/2	Rubber

/1/ Product consists of a small amount of rubbery material (0.4%) and a major portion of granular material. The analysis applies to the granular material. This latter material has not been further investigated.

FILE NO. LAS-105
FJH:SB 1-5-54

TABLE 6

CF_2=CFCl/CF_2=CH_2/X TERPOLYMERS

Recipe: persulfate-bisulfite-Iron
Suspension, 20°C.

Run No.	Termonomer (X)	Moles Charged	Moles Found	% Conversion	Hrs. Polymerization	Appearance
1295	diethyl fumarate	40/40/20	-	0	24	-
1296	diethyl maleate	40/40/20	-	0	24	-
1297	Cl-CH_2-CO-O-CH=CH_2	40/40/20	/1/	53	24	V. sl. rubbery
1315	CH_3-CH_2-CH_2-CO-O-CH=CH_2	48/48/4	50/46/4	44	1/4	like X-300
1316	CH_3-CH_2-CH_2-CO-O-CH=CH_2	40/40/20	41/39/20	36	1/4	slow, stiff rubber
1278	CH_3-CO-O-CH=CH_2	47.5/47.5/5.0	45/48/7	30	1/6	hard, rubbery crumb
1195	CH_3-CO-O-CH=CH_2	40/40/20	35/45/20	43	1/2	powder
1281	CH_2=CHCl	47.5/47.5/5.0	-	6.5	2	powder
1200	CH_2=CHCl	40/40/20	/2/	23	24	powder
1138	CH_2=CFCl	15/65/20	/3/	86	5	rubber
1235	C_6H_5-CH=CH-CO_2CH_3	40/40/20	-	0	24	

/1/ 24.0% Cl, 34.0% F; one possible ratio is 40/32/28.
/2/ 45.0% Cl, 26.2% F.
/3/ 18.9% Cl, 47.0% F; one possible ratio is 14/60/26.

FILE NO. LAS-104
FJH:SB 1/7/54

TABLE 7

MISCELLANEOUS EXPLORATORY COPOLYMERIZATIONS

Run No.	Comonomers	Moles Charged	Moles Combined	Recipe	% Conversion	Hrs. Polymerization	Appearance
1210	$CF_2=CF-CF=CF_2/CH_3CO-OCH=CH_2$	50/50	26/74	/a/	21	24	powder
1219	$CF_2=CF-CF=CF_2$ alone	100/0	-	/b/	0	48	-
1203	$CF_2=CF-CF=CF_2$ distillation tail on standing 3 months at -70°C.	-	F found 47.8% F thio. 70.4% no Cl present				rubber
1274	$CF_2=CF-CF=CF_2/CH_2=CFCl$	50/50	-	/a/	trace	24	white solid
1277	$CF_2=CF_2$/n-butyl acrylate	50/50	18/82	/a/	64	24	tacky, short rubber
1300	$CF_2=CF-CF=CF_2/SO_2$	20/80	-	/c/	0	16	-
1236	$CF_2=CFCl/CH_2=CH-Si(OC_2H_5)_3$	50/50	-	/d/	0	48	-

/a/ Persulfate-bisulfite-iron suspension, 20°C.
/b/ 1% azodi-isobutyronitrile, 24 hrs. at 40°, 24 hrs. at 60°.
/c/ 1% benzoyl peroxide, 60°C.
/d/ 2% azodi-isobutyronitrile, 50°C.

FILE NO. LAS-110
FJH:SB 1/7/54

TABLE 8

COMPOUNDING X-300 RUBBER

QM Code	13F28	13F29	13F32	13F37	13F57	13F58	13F59	13F60	6F5	6F12	6F13	16F22	13F46	13F48	13F50	13F53	13F55	13F56	6F3	6F4
X-300 50/50	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5		5	5	5	5		5	5	5				5	5	5		5	5
MDI-100 /1/	5		5	5	5	5	5	5							5	5	5			
TETA /2/	1	1	1											5	3					
Kellogg Curative 180-56		5																		
Urotropine /3/					5			5								1	3	5		
Trimal /4/						5														
Hepteen Base /5/							5													
Kellogg Curative 180-108									5											
Kellogg Curative 212-90										5										
Kellogg Curative 212-98											5									
Benzoyl Peroxide												1.5								
Diethyl oxylate													5							
Na methylate													1							
Kellogg Curative 180-100																			5	
Kellogg Curative 180-104																				5

/1/ Pure Grade methylene-bis (p-phenyl isocyanate).
/2/ Tri ethylene tetramine.
/3/ Hexamethylene tetramine.
/4/ Tri basic lead maleate
/5/ Heptaldehyde aniline condensate.

FILE NO. MM-865
LER:MM 9-4-53

TABLE 9

PHYSICAL PROPERTIES OF CURED X-300

Compound No.	Press Cure hr./°F.	Oven Cure hr./°F.	Mod. 300% psi	T.S.	% E.	Appearance of Stock
13F28	1/260	16/212	1350	1700	330	Good
13F29	"	None	1150	1375	350	"
13F32			400	900	610	"
13F37	"	"	790	830	310	"
13F57	1/290	None	300	900	900	Fair
13F58	1/290	"	300	680	1200	Good
13F59	1/290	"	300	720	1300	Bubbles
13F60	1/290	"	650	1100	400	Good
6F5	1/260	16/212	550	900	445	
6F12	1/260	16/212	600	800	365	
6F13	1/260	16/212	650	1100	415	
16F22	½/230	16/350	-	500	-	
13F46	1/260	16/212	-	280	600	Fair
13F48	1/260	16/212	980	1590	410	Good
13F50	"	"	1250	1250	300	"
13F53	"	"	250	390	406	"
13F55	"	"	625	1250	390	"
13F56	"	"	-	250	1300	"
6F3	"	"	-	550	1100	"
6F4	"	"	-	500	1150	"

FILE NO. MM-861
LER:MM 9-4-53

TABLE 10

CURRENT STATUS OF RUBBER-LIKE POLYMERS
(See end of table for Monomer Identification)

Raw Polymer Screening Tests

Run No.	Monomer Combination	Mole Ratio Combined	% Conversion	Appearance	Gehman Stiffness, °C. T_2	T_5	T_{10}	T_{100}	% Volume Increase, Type II Fuel	Mold Temp. °F.	Sample Condition after Molding
X-300	1-2	50/50	--	rubber	7	5	4	-2	18	300	soft, flex.
X-300	1-2	30/70	--	rubber	-10	-15	-17	-26	5	300	soft, flex.
1021 (1)	1-2-14	43/53/4	75-80	short rubber	6	4	3	-7	8	--	----
1190	1-2-21	44/40/16	19	rubber	9	7	6	-1	22	225	hard, flex.
909	1-2-22	56/8/36	24	slow rubber	15	11	10	7	gel	225	soft, flex.
970	1-2-22	39/36/25	85	short, fast rubber	13	8	7	4	64	225	soft, flex.
1138	1-2-22	15/65/20 /2/	86	rubber	shipped for test						
	1-2-23				no test						
	1-2-24				no test						
	1-2-29				no test						
955	1-2-30	39/38/23	54	slow rubber	24	19	18	15	gel	225	soft, vitreous
770	1-2-32	40/40/20 /2/	78	rubber	shipped for test						----
987	1-2-33	49/51/Trace	44	rubber	10	8	6	0	32	225	hard, flex.
	1-2-34				no test						
1088	1-2-40	52/48/Trace	32	slightly rubbery	20	18	17	15	31	225	hard, flex.
1278	1-2-45	45/48/7	30	hard, rubbery crumb	shipped for test						
1315	1-2-45a	50/46/4	44	like X-300	shipped for test						
1316	1-2-45a	41/39/20	36	slow, stiff rubber	shipped for test						
1297	1-2-45b	40/32/28	53	v. slightly rubbery	no test						
	1-3			already rejected because of poor oil-resistance							
	1-5			already rejected because of poor oil-resistance							
	1-13			no test							
	1-17			no test: QM could not	large 30/70 batch (run no. 742)						
763	1-17a	35/65	72	slightly rubbery	no test						
750	1-21	63/37	4	slightly rubbery	no test						
	1-22			no test							
	1-28			no test impure 28							
1012	1-37	15/85	38	short, weak rubber	-2	-16	-17	-23	50	300	soft, flex.
1004	1-41	11/89	53	fast rubber	-6	-15	-19	-25	122	225	soft, flex.
1218	1-43	1/99	37	fast rubber	no test, too little monomer 1 combined						
1221	1-44	25/75	54	rubber	shipped for test						
	1-45a				no test						
1331	1-47	51/49	59	v. slightly rubbery	shipped for test						
1040	35-37	23/77	30	med. rubber	8	-16	-22	<-65	28	300	hard, stiff
	35-40			no test							
1252	35-43	14/86	40	stiff rubber	shipped for test						
1231	35-44	1/99	38	soft rubber	no test, insufficient 35 combined						
1090	37-39	84/16	42	soft rubber	15	0	-1	-16	60	225	soft, flex.
1049	37-41	80/20 /4/	92	soft rubber	-17	-26	-28	-32	70	300	soft, flex.
1251	37-43	10/90 /4/	100	rubber	shipped for test						
1157	38-41	1/99	32	soft, snappy rubber	no test, insufficient 38 combined						
1237	38-44	4/96	40	soft, weak rubber	no test, insufficient 38 combined						
1010	39-41	16/84	29	soft, slow rubber	insufficient sample for screening test						
1232	39-44	19/81	35	slow rubber	shipped for test						
1011	41	--	104	tough, fast rubber	-15	-21	-25	-29	111	250	soft, flex
1160	41-42	99/1	45	soft, slow rubber	no test, insufficient 42 combined						
1249	41-43	10/90 /4/	32	rubber	shipped for test						
1233	41-44	--	94	rubber	shipped for test						
1253	43	--	94	stiff rubber	shipped for test						
1254	43-44	97/3 /4/	80	rubber	shipped for test						
	44			no test, has not been prepared							

/1/ Tests conducted with vulcanized sample.
/2/ Mole ratio in monomer feed.
/3/ Constant pressure runs.
/4/ Reason for unexpected analytical results undetermined.

Monomer Identification

Code No.	Monomer	Code No.	Monomer	Code No.	Monomer	Code No.	Monomer
1	$CF_2=CFCl$	14	$CF_3-CF=CF_2$	26	$CH_2=CH-C_6H_4-CH=CH_2$	39	$CF_3-CCl=CH_2$
2	$CH_2=CF_2$	15	$CF_2=CF-CN$	27.	$CH_2=C\begin{smallmatrix}CH_3\\CF_3\end{smallmatrix}$	40	$CH_2=CHF$
3	$CH_2=CH-CH=CH_2$	16	$CH_2=CH-CN$	28	$CH_2=CF-CH=CH_2$	41	$CF_2=CH-C(CH_3)=CH_2$
4	$CF_2=CF-CF=CF_2$	17	$CH_2=CH-CO_2-C_4H_9(n)$	29	$CF_2=C\begin{smallmatrix}CF_3\\CF_3\end{smallmatrix}$	42	$CF_3-CH=CF_2$
5	$CH_2=C(CH_3)-CH=CH_2$	17a	$CH_2=CH-CO_2-CH_3$	30	$CF_2=CFBr$	43	$CF_3-CH=CH-CH=CH_2$
6	$(CH_3)_2C=CH_2$	18	$CF_2=CHCl$	31	$CH_2=CH_2$	44	$CF_2=C(CH_3)-CH=CH_2$
7	$\underline{CF_2-CF=CF-CF_2}$	19	$CF_3-CCl=CCl-CF_3$	32	$CF_3-CCl=CF_2$	45	$CH_2=CH-O-CO-CH_3$
8	$CH_2=CHCl$	20	$CF_3-C\equiv C-CF_3$	33	$CH_3-C(CF_3)=CH-COOH$	45a	$CH_2=CH-O-CO-CH_2-CH_2-CH_3$
9	$CF_2=CCl_2$	21	$CF_2=CFH$	34	$CH_2=CH-CO-NH_2$	45b	$CH_2=CH-O-CO-CH_2Cl$
10	$CH_3-CH=CH_2$	22	$CH_2=CFCl$	35	$CF_3-CH=CH_2$	46	$C_6H_5-CH=CH-CO_2CH_3$
11	$C_6H_5-CH=CH_2$	23	cis - $CF_3-CH=CH-CF_3$	36	$CH_2=CHBr$	47	$CH_2=CH-O-CH_2CH_3$
12	$CH_2=CCl_2$	24	$CF_2=CF_2$	37	$CF_2=CH-CH=CH_2$	48	$CH_2=CH-O-CH_2-CH_2Cl$
13	$CH_2=CCl-CH=CH_2$	25	trans - $CF_3-CH=CH-CF_3$	38	$CF_3-CCl=CCl_2$	49	$CH_2=CH-O-CH_2-CH(CH_3)_2$
						50	$CF_2=C(CH_3)-CF=CH_2$
						51	$CF_2=CH-CF=CH_2$

FTL-6 NO. LAB-35
AMH:LAB 9-2-53

THE M. W. KELLOGG COMPANY
Petroleum & Chemical
Research Dept.
Jersey City, N. J.

Report No. RL-5

TABLE 10

CURRENT STATUS OF RUBBER-LIKE POLYMERS
(See end of table for Monomer Identification)

Raw Polymer Screening Tests

Run No.	Monomer Combination	Mole Ratio Combined	% Conversion	Appearance	Gehman Stiffness, °C. T_2	T_5	T_{10}	T_{100}	% Volume Increase, Type II Fuel	Mold Temp. °F.	Sample Condition after Molding
X-300	1-2	50/50	--	rubber	7	5	4	-2	18	300	soft, flex.
X-300	1-2	30/70	--	rubber	-10	-15	-17	-26	5	300	soft, flex.
1021 (1)	1-2-14	43/53/4	75-80	short rubber	6	4	3	-7	8	--	----
1190	1-2-21	44/40/16	19	rubber	9	7	6	-1	22	225	hard, flex.
909	1-2-22	56/8/36	24	slow rubber	15	11	10	7	gel	225	soft, flex.
970	1-2-22	39/36/25	85	short, fast rubber	13	8	7	4	64	225	soft, flex.
1138	1-2-22	15/65/20 (2)	86	rubber	shipped for test						
	1-2-23				no test						
	1-2-24				no test						
	1-2-29				no test						
955	1-2-30	39/38/23	54	slow rubber	24	19	18	15	gel	225	soft, vitreous
770	1-2-32	40/40/20 (2)	78	rubber	shipped for test						----
987	1-2-31	49/51/Trace	44	rubber	10	8	6	0	32	225	hard, flex.
	1-2-34				no test						
1088	1-2-40	52/48/Trace	32	slightly rubbery	20	18	17	15	31	225	hard, flex.
1278	1-2-45	45/48/7	30	hard, rubbery crumb	shipped for test						
1315	1-2-45a	50/46/4	44	like X-300	shipped for test						
1316	1-2-45a	41/39/20	36	slow, stiff rubber	shipped for test						
1297	1-2-45b	40/32/28	53	v. slightly rubbery	no test						
	1-3			already rejected because of poor oil-resistance							
	1-5			already rejected because of poor oil-resistance							
	1-13			no test							
	1-17			no test: GM could not	large 30/70 batch (run no. 742)						
763	1-17a	35/65	72	slightly rubbery	no test						
750	1-21	63/37	4	slightly rubbery	no test						
	1-22			no test							
	1-28			no test, impure 28							
1012	1-37	15/85	38	short, weak rubber	-2	-16	-17	-23	50	300	soft, flex.
1004	1-41	11/89	53	fast rubber	-6	-15	-19	-25	122	225	soft, flex.
1218	1-43	1/99	37	fast rubber	no test, too little monomer 1 combined						
1221	1-44	25/75	54	rubber	shipped for test						
	1-45a				no test						
1331	1-47	51/49	89	v. slightly rubbery	shipped for test						
1339	1-48	60/40	52	hard, slow rubber	shipped for test						
	1-49				no test						
	2-4				no test						
	2-6				no test						
	2-13				no test						
	2-17				no test						
1081	2-22	48/52	74	slightly rubbery	9	0	-3	-22	24	225	hard, stiff
572	2-24	35/65	57	v. slightly rubbery	-13	-70	<-75	<-75	1	425	hard, stiff
	2-28				no test, impure 28						
698	2-29	38/62	2	slightly rubbery	no test						
695	2-30	55/45	50	rubber	sample shattered in dye				gel		
	2-32				no test						
	2-34				no test						
1215	2-43				no test						
1211	2-44	10/90	38	rubber	shipped for test						
567	3-4	79/21	27	rubbery crumb	-50	-62	-65	<-66	396	300	soft, flex.
568	3-4	76/24	27	rubbery crumb	-23	-51	-58	<-60	427	300	soft, flex.
515	3-4	71/29	22	tacky rubber	-15	-29	-38	-50	314	300	soft, flex.
291	3-4	66/34	82	rubbery crumb	-31	-41	-42	-54	Fell apart, cheesy		milled
290	3-4	60/40	48	rubbery crumb	-17	-29	-33	-42	Fell apart, cheesy		not molded
	3-9			already rejected, poor oil resistance							
	3-14			no test							
EYCAR OR-15	3-16	65/35	--	----	2	-10	-13	-17	32	300	soft, flex.
	3-18			no test							
	3-19			no test							
	3-21			no test							
	3-22			no test							
	3-23			no test							
573	3-24	86/14	23	rubbery crumb	5	-18	-38	<-60	588	300	soft, flex.
522	3-24	81/19	28	rubber	-6	-25	-42	-57	367	300	soft, flex.
576	3-24	76/24	16	rubbery crumb	5	-8	-27	-56	393	300	soft, flex.
670	3-32	80/20	48	rubber	no test						
1222	3-44	52/48	83	soft rubber	shipped for test						
1203	4	rubbery residue from $CF_2=CF-CF=CF_2$ tank								42.7% F.	
		theoritical % F. for $CF_2=CF-CF=CF_2$ is 70.4.									
	4-5			already rejected, poor oil resistance							
	4-28			no test, impure 28							
1013	4-37	32/68	43	stiff, short rubber	10	-10	-17	-29	38	300	hard, stiff
1005	4-41	14/86		fast, snappy rubber	0	-10	-20	-28	114	225	soft, flex.
1243	4-43	18/82	41	stiff rubber	shipped for test						
1272	4-44	12/88	29	slow rubber	shipped for test						
1341	4-48	15/85	50	rubber	shipped for test						
1306	4-49	52/48	96	short rubber	shipped for test						
	5-9			already rejected, poor oil-resistance							
1227	5-44	50/50	86	sl. tacky rubber	shipped for test						
1036	6-37	1/99	30	soft, slow rubber	no test, low 6 content						
1140	6-41	15/85	48	soft, fairly slow rubber	no test						
1037	7-37	4/96	29	hard rubber	no test, low 7 content						
1139	7-41	7/93	40	soft, snappy rubber	test sample charred in mold					300	
1255	7-43	6/94	10	rubber	shipped for test						
1293	7-44	1/99	16	slow rubber	no test, low 7 content						
1039	8-37	21/79	27	soft, slow rubber	20	13	5	-9	59	225	soft, tacky
1141	8-41	9/91	56	soft, snappy rubber	5	-6	-12	-23	gel	200	soft, tacky
1296	8-44	18/82	49	soft rubber	shipped for test						
	9-12			no test							
	9-13			no test							
	9-17			no test							
	9-28			no test, impure 28							
1015	9-37	16/84	43	tough, v. elastic rubber	-1	-14	-18	-22	64	300	soft, flex.
1006	9-41	12/88	65	fast, snappy rubber	5	-5	-12	-23	gel	225	soft, flex.
1244	9-43	11/89	38	slow rubber	shipped for test						
1274	9-44	22/78	50	rubber	shipped for test						
1305	9-49	44/56	9	hard, v. sl. rubbery	no test						
	12-28			no test, impure 28							
	12-37			no test							
	12-41			no test							
	13-18			no test							
	14-22			no test							
	14-28			no test, impure 28							
1036	14-37	8/92	27	hard rubber	no test						
1143	14-41	2/98	69	soft, fast rubber	no test, low 14 content						
1245	14-43	21/79	42	stiff rubber	shipped for test						
1291	14-44	2/98	22	slow rubber	no test, low 14 content						

TABLE 11

COPOLYMERS TO BE SCREENED FOR OIL RESISTANCE
AND LOW TEMPERATURE FLEXIBILITY

COPOLYMERS OF $CF_2=C(CH_3)-CH=CH_2$ (DFI)

Run No.	Comonomer	Mole % ratio DFI/Comonomer	% Conversion
1221	$CF_2=CFCl$	75/25	54
1222	$CH_2=CH-CH=CH_2$	48/52	83
1225	$CF_3-C(CH_3)=CH_2$	91/9	33
1226	$CH_2=CHCl$	82/18	49
1227	$CH_2=C(CH_3)-CH=CH_2$	50/50	86
1229	$CH_2=CH-CN$	88/12	79
1232	$CF_3-CCl=CH_2$	81/19	35
1233	$CF_2=CH-C(CH_3)=CH_2$	?	94
1234	$CF_3-CH=CH_2$	82/18	32
1240	$n-CH_2=CH-C(=O)-OC_4H_9$	52/48	91
1272	$CF_2=CF-CF=CF_2$	88/12	29
1273	$CF_2=CCl_2$	78/22	50
1211	$CH_2=CF_2$	90/10	38
1212	$CF_2=CF_2$	90/10	49
1213	$CF_2=CFH$	90/10	49

COPOLYMERS OF $CF_3-CH=CH-CH=CH_2$

Run No.	Comonomer	Mole % ratio	% Conversion
1243	$CF_2=CF-CF=CF_2$	82/18	41
1244	$CF_2=CCl_2$	89/11	38
1245	$CF_3-CF=CF_2$	79/21	42
1246	$CH_2=CFCl$	81/19	51
1249	$CF_2=CH-C(CH_3)=CH_2$	90/10	92
1251	$CF_2=CH-CH=CH_2$	90/10	100
1252	$CF_3-CH=CH_2$	86/14	40
1253	none	100/0	94
1254	$CF_2=C(CH_3)-CH=CH_2$	97/3	80
1215	$CF_2=CF_2$	86/14	48

Run No.	Comonomers	Mole % Combined	% Conversion
1348	$CF_2=CF_2$/vinyl ethyl ether	48/52	41
1317	$CF_2=CF_2$/vinyl butyrate	35/65	16
1340	$CF_2=CF_2$/vinyl 2-chloroethyl ether	49/51	39
1328	$CF_2=CF_2/CH_2=CFCl$	32/68	/a/
1313	$CF_2=CF_2/CH_2=CFCl$	50/50	/a/
1347	$CF_2=CF_2/CH_2=CFCl$	65/35	/a/
1339	$CF_2=CFCl$/vinyl 2-chloroethyl ether	60/40	52
1331	$CF_2=CFCl$/vinyl ethyl ether	51/49	89
1341	$CF_2=CF-CF=CF_2$/vinyl 2-chloroethyl ether	15/85	50
770	$CF_2=CFCl/CF_2=CH_2/CF_3-CCl=CF_2$	40/40/20 /b/	78
1278	$CF_2=CFCl/CF_2=CH_2$/vinyl acetate	45/48/7	30
1315	$CF_2=CFCl/CF_2=CH_2$/vinyl butyrate	50/46/4	44
1316	$CF_2=CFCl/CF_2=CH_2$/vinyl butyrate	41/39/20	36
1203	Residue from $CF_2=CF-CF=CF_2$	47.2% F no Cl /c/	-
1277	$CF_2=CF_2$/n-butyl acrylate	18/82	64
1304	$CF_2=CF_2$/vinyl isobutyl ether	50/50	41
1306	$CF_2=CF-CF=CF_2$/vinyl isobutyl ether	52/48	96
1138	$CF_2=CFCl/CF_2=CH_2/CH_2=CFCl$	/d/	56
1081	$CF_2=CH_2/CH_2=CFCl$	48/52	74
987	$CF_2=CFCl/CF_2=CH_2/CH_2=CH_2$	49/51/trace	44
1088	$CF_2=CFCl/CF_2=CH_2/CH_2=CHF$	52/48/trace	32
1190	$CF_2=CFCl/CF_2=CH_2/CF_2=CFH$	44/40/16	19

/a/ Constant feed runs.
/b/ Mole % ratio of monomers charged.
/c/ This material is of unknown structure. Theoretical % F for poly-perfluorobutadiene is 70.4.
/d/ Charge ratio 15/65/20

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